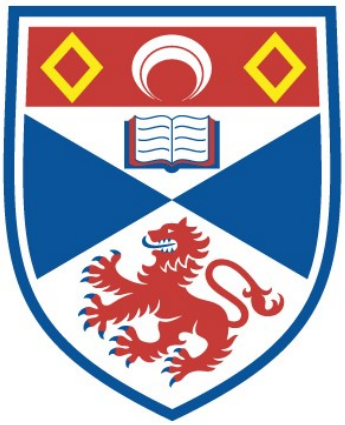
AROMATIC SYSTEMS CONTAINING THE PERINAPHTHENE NUCLEUS

Ian Morrison Aitken

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1958

AROMATIC SYSTEMS CONTAINING THE PERINAPHTHENE NUCLEUS.

being a Thesis presented by

IAN M. AITKEN.

to the University of St. Andrews in

application for the degree Ph. D.

CERTIFICATE.

I certify that Ian M. Aitken has spent nine terms at research work under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying Thesis in application for the degree of Ph. D.

Director of Research.

19th May. 1958.

DECLARATION.

I hereby declare that the following Thesis is a record of the results of experiments carried out by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Chemical Research Department of the University of St. Andrews under the direction of Dr. D. H. Reid.

19th May, 1958.

ACKNOWLEDGMENTS.

I should like to express my sincere gratitude to Dr. D.H.Reid of the Chemistry Department of St. Andrews University for assistance and guidance given me during the prosecution of the work embodied in the present thesis. Throughout the course of the investigation, Dr. Reid proved, at one and the same time, to be well versed in and have remarkable insight into the theories and practice of organic chemistry, and yet be an able exponent of laboratory technique and possess an ability to transmit his own enthusiasm for his subject to his pupils.

I am indebted to my father, Mr. Thomas Aitken of Glasgow, for his help and encouragement during the course of my studies; but in particular with reference to the first year when, in the absence of any grant or scholarship from any source whatsoever, he chose generously to bear the entire financial burden associated with my maintenance. Without his unstinted aid it would, of course, have been impossible to undertake this work.

I am grateful to the Department of Scientific and Industrial Research for the award of a Research Studentship to cover the latter two years of my research programme.

I should like to thank the various members of the Technical Staff of St. Andrews University who gave of their services in connection with the experimental aspect of the work, and especially to Mr. R. Morris and Mr. M. Zochowski of the Chemistry Department, and Mr. E. Noseman of the Natural Philosophy Department.

In conclusion, I must pay tribute to Miss Paterson of Glasgow, who undertook the bulk of the typewriting, for her co-operation in the somewhat perplexing task of preparing the manuscript of a chemical thesis.

University of St. Andrews.
May, 1958.

UNIVERSITY CAREER.

I first matriculated in the United College of St. Salvator and St. Leonard, University of St. Andrews, in October 1949, and subsequently obtained the degree of B.Sc. with Second Class Honours in Chemistry in June 1954.

I was admitted as a Research Student in the Chemistry Department of the above University in October 1954.

I was awarded a Research Studentship under the sponsorship of the Department of Scientific and Industrial Research covering the period 1955-57.

EXPLANATORY NOTE.

This thesis comprises three parts, Parts A, B and C. Each part is divided into a number of principal sections prefixed by Roman numerals, and these sections are further divided into sub-sections prefixed by Arabic numerals. Each sub-section is uniquely indicated by a combination consisting of a capital letter, a Roman and an Arabic numeral, e.g., (A,IV,1) - Perinaphthene System: Nomenclature.

Part A commences with a brief analytical survey based on the Chemical Literature of the various aromatic carbocyclic systems, and this is developed logically into a consideration of the perinaphthene system. A detailed review of the latter and its simple derivatives follows, with particular emphasis on the theoretical aspects of this system.

Part B is an account of the results achieved by the author in the course of investigations centred on aromatic compounds containing the perinaphthene nucleus. The synthesis and properties of indeno[2,1-a]perinaphthene are described, in addition to preliminary experiments with a view to preparing cyclopenta[a]-perinaphthene. The outcome of the investigation is fully examined from the theoretical standpoint.

Part C is entirely devoted to experimental details, and is the complement to Part B. Ten plates, mainly of absorption spectra, are to be found at the end of the thesis.

Where reference is made to the Chemical Literature, this is indicated by a number in superscript, a key to which will be found at the end of the appropriate Part under the section headed 'Literature cited'. When a fact is stated or an opinion expressed to which no literature reference applies, it must be assumed that these have their origin in the experimental work or the personal views respectively of the author.

CORRECTION.

Unfortunately, a discontinuity has occurred in the numbering of formulae in Part A. Thus formula number (339) is followed by formula number (400), and there are no formulae corresponding to numbers (340) - (399) inclusive. Notwithstanding this error, numbers in the text are accurately related to these appearing on formulae, and provided the above is borne in mind, no difficulty should be experienced in referring to the latter.

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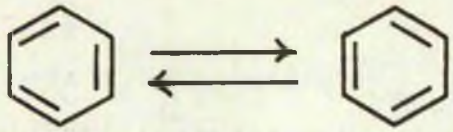
PART A.

A.1. EARLY IDEAS ON THE NATURE OF AROMATIC STABILITY.

A.I.1. Early Theories on Benzene.

Aromatic chemistry may be said to have had its beginning in the classical hypotheses of Kekulé in 1856[1] on the structure of benzene, for which he proposed a six-membered carbocyclic system containing alternate single and double bonds between the constituent carbon atoms as the fundamental unit of a group of compounds whose structure could not be elucidated by the then known rules of aliphatic chemistry. Unfortunately, these postulates, though solving some problems of a structural nature, created many more of a theoretical nature; problems which, it cannot be said, are properly solved today over ninety years later.

The following years of the nineteenth century are noted for intense activity, both in the experimental field in the building up of the main framework of aromatic chemistry, and in the speculative field in connection with the assignment of a suitable formula to this new molecular species, the numerous papers by Baeyer, Armstrong, Dewar, Graebe, Claus, Ladenburg and their contemporaries testifying to this. It suffices at this stage to state that, arising out of their work, benzene was shown to be a monocarbocyclic system, which, though it could only be shown by conventional formulae to possess considerable formal unsaturation, nevertheless underwent substitution rather than addition reactions, and possessed stability not in keeping with an olefinic compound and showed a great tendency to retain type. Furthermore all the six positions appeared to be equivalent and no substituted isomers of the type demanded by the Kekulé formula could be isolated. It fell to Kekulé to make yet another fundamental hypothesis, and in 1872[2] he proposed that in view of the fact that benzene could not be represented by any single formula which was in accord with its observed properties, particularly its symmetry in substitution reactions, it must be regarded as possessing a formula which involved oscillation between the two possible arrangements of double bonds (1).



(1)

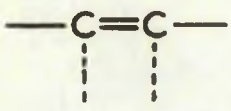
It is a tribute to his foresight, that in the current concept of the 'mesomeric' state of benzene, Kekulé's ideas have undergone modification rather than total abandonment.

Amongst the many pre-electronic theories on the structure of benzene, one concept other than Kekulé's calls for special mention, that of Dewar[3] which involves two double bonds and what might be termed a 'para' bond (2).

(2)

Dewar's concept of a single structure of this type is, of course, as equally unsatisfactory as Kekulé's original non-oscillating structure. The possibility that structures of this type might, however, oscillate with the Kekulé structures was raised by Ingold[4], and Pauling and Wheland[5] using the valence bond approximation to determine the molecular diagram for benzene, consider the hybrid to be made up of a contribution of 22% of all the possible Dewar structures, the latter condition being imposed to maintain the characteristic symmetry. The 'para' bonds in benzene and its fused ring homologues have been used as a diagrammatic representation of the somewhat abstruse valence bond (and also molecular orbital) approximation term, 'free valence'.

In this brief account of the pre-electronic theories of the structure of benzene it is relevent to give passing mention to the theory of partial valences and conjugation as put forward by Thiele[6],



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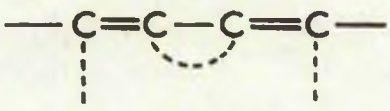

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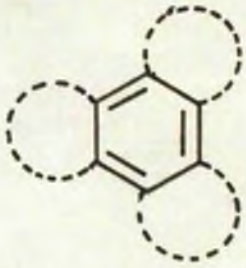

(5)

who considered that each carbon atom had four 'affinities' for combination. A double bond had six 'affinities' neutralised, and two residual 'affinities' or partial valences shown as dotted lines (3) on adjacent carbon atoms, thus explaining its additive capacity. In a conjugated system such as butadiene, the partial valences on the central carbon atoms were considered by Thiele to be mutually satisfied, as in (4). By extension to a cyclical conjugated system such as benzene, a unique state is developed where mutual satisfaction is complete (5), and residual affinity, or double bond character, is absent. The theory had the advantage in explaining 1:4 addition to diene systems, but all examples of 1:2 additions formed exceptions to the rule which was incapable of embracing even a majority of them, though it is important in recognising some similarity in the lowered reactivity of double bonds in conjugated systems, and the considerably lowered reactivity of double bonds in aromatic compounds.

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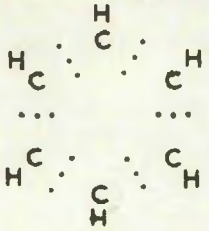
A,I,2. The 'Aromatic Sextet'.

The development of the electronic concept of valency by Thomson[7], Lewis[8], and Langmuir[9] cleared the ground for a more satisfactory explanation of aromatic character. Chemists had, of course, previously been trying to find some uniform explanation to account for this phenomenon and, for instance, Bamberger[10] (1890) took the standpoint of the requirement of six 'potential valencies' for the creation of the aromatic state. Thomson was the first to attempt to visualize benzene in terms of the newer electronic theories in his formula (6) involving the sharing of three electrons by two atoms.



(6)

(7)

(8)

The most fundamental and lasting concepts regarding the theory of aromaticity at this time were those made in a series of publications by Robinson and his co-workers on the electronic basis

of organic reactions and related matters. It does seem reasonable, that as an extension of the hypothesis that certain electronic configurations around the atom or between two bonded atoms are stable, e.g. the octet and duplet respectively, that this hypothesis should have some counterpart on the molecular scale where electrons are associated with a group rather than with individual atoms. Such an idea was foreshadowed[11][12], and finally proposed in the classical work on the subject by Armit and Robinson[13] in which the concept of the 'aromatic sextet' was introduced, a stable association of six valency electrons which conferred upon the system chemical stability. Such an arrangement of electrons is not capable of representation by formulae involving chemical bonds, and Robinson proposed the now well known symbols (7) and (8) to express this new formulation.

The great value of the concept of the 'aromatic sextet' is that it was simultaneously applicable in the consideration of aromatic systems other than benzene e.g. the simpler heterocyclic molecules, and could also be used in predicting inherent aromatic stability in systems as yet unknown. Robinson, in his original ideas, placed no restriction on the source of the 'sextet' electrons which could be supplied by the spare valency electrons of elements, such as nitrogen or sulphur, thus giving a qualitative theoretical expression of the observed properties, i.e., acidity or basicity of these elements, in such chemical combination. Robinson did not suggest abandonment of the Kekulé type structures, and the considerable gradation of 'reduced unsaturation' that is observed as one passes through even the simple monocycles must be taken as indicative of the fact that these structures must be present to a greater or lesser extent in the reacting molecule if not in the normal state.

A.I.3. Application of the 'Aromatic Sextet' to Heterocyclic Systems.

It is important at this stage to consider briefly the application of the concept of the 'aromatic sextet' to the simpler monocyclic heterocyclic systems and how it accounts in a qualitative sense for the properties of these systems. The origin of the six

electrons in thiophen, pyrrole and furan is as shown in (9),(10) and (11). We might expect, as a consequence of the involvement of the 'spare' valency electrons in the 'sextet' instability towards acids,

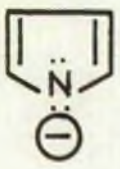
(9)

(10)

(11)

which would utilise these electrons in electrovalent bond formation. This is borne out in practice, and both pyrrole and furan show instability towards acids, undergoing polymerisation (c.f. cyclopentadiene); exceptionally, however, thiophen is stable in acid media. The sulphur atom in thiophen, which is the most stable member of the trio, does not react as a sulphide, being oxidised neither to a sulphoxide nor to a sulphone, nor does it give sulphonium salts with alkyl halides.

The sharing of six electrons by five atoms would be expected to confer a high degree of nucleophilicity, and all the above compounds are generally more susceptible to electrophilic attack, than, for instance, benzene, with the reservation, of course, that strong acids be absent. This property has led some authors to use the term 'super aromatic' with regard to these compounds; a term which, in view of other properties such as the ability of pyrrole and furan to act as dienophiles in the Diels-Alder reaction, a property of dienes, can be regarded as extremely unfortunate. In view of the greater electron availability in the vicinity of the hetero atom, electrophilic attack manifests itself mainly at the α-carbon atom.



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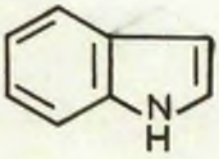

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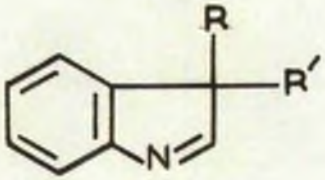
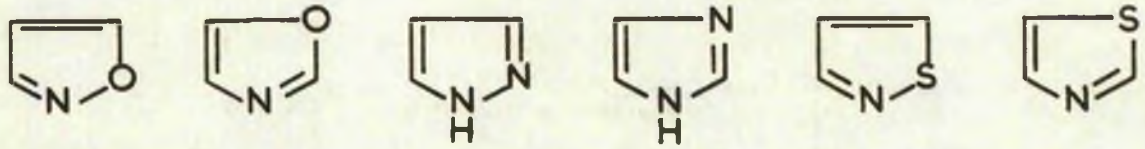


(14)

As a consequence of the reduced accessability of the spare pair of electrons of the nitrogen atom for salt formation, the latter element would not be expected to confer any basic properties on pyrrole. In the formation of the anion (12) on the contrary, the internal electronic structure is maintained, and pyrrole displays acidic properties forming a potassium derivative both with potassium hydroxide and with metallic potassium, a property exhibited by the carbocylic analogue cyclopentadiene. The pyrrole potassium derivative will actually undergo N-acylation and alkylation, but the products rearrange on heating to the more stable substituted derivatives. Indole (13) is likewise acidic, a property which does not pertain in indolenine (14) where the β-carbon atom is disubstituted, thus interrupting the conjugation. Indolenines are very much less stable than the corresponding indoles, and in contrast to the latter, are basic.

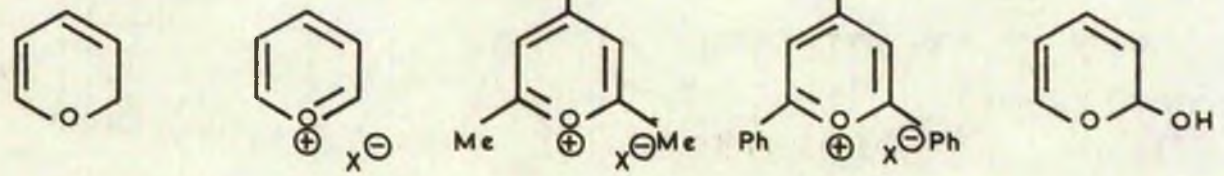


(15) (16) (17) (18) (19) (20)

The five membered analogues of pyrrole containing two hetero atoms i.e. oxazole (15), iso-oxazole (16), imidazole (17), pyrazole (18), thiazole (19), and iso-thiazole (20) are all able to derive valency electrons from their constituent atoms to form a 'sextet', and all show greater or lesser aromatic stability on this account. One salient feature, however, serves to distinguish them from pyrrole; they are all capable of forming salts with strong acids, acting as mono-acidic bases, though exceptionally oxazole and iso-oxazole are decomposed in boiling acid. This property can be attributed to the fact that at least one nitrogen atom in each compound is capable of using its spare valency electrons for salt formation, as opposed to contributing these electrons to the election 'sextet'.

(21)

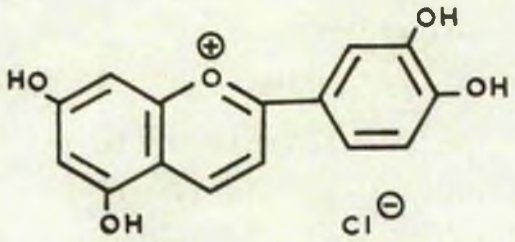
In the case of the six-membered monocyclic compounds containing one hetero-atom, the 'aromatic sextet' is built up by the uniform contribution of one electron from each constituent atom. In the case of pyridine (21) such a contribution does not consume the spare valency electrons which are therefore available for salt formation. Pyridine is thus weakly basic, and also forms quaternary salts with reactive halides. The electronic arrangement of the six electrons in pyridine must approach more closely that in benzene than does that of pyrrole, and as a consequence this compound shows much greater stability than its lower analogue, being in some respects more stable than benzene. The greater electronegativity of nitrogen relative to carbon, however, results in a considerable modification of the nucleophilicity of the carbon atoms of pyridine as compared to benzene, so comparison cannot be pushed too far.



(22) (23) (24) (25) (26)

In forming a sextet from the pyran molecule (22) one is at once faced with the problem that oxygen cannot contribute an electron without becoming positively charged (23). Tervalent oxygen would not be expected to be so stable as the divalent forms, and ethers are only very weak bases. This loss in stability can be counterbalanced by a corresponding gain in the formation of the 'sextet'. The resultant stability achieved, however, is not comparable to that found in pyridine, and originally only substituted pyrylium salts e.g. (24) and (25) were known though pyrylium perchlorate has now been prepared. The pyrylium cation is only stable in the presence of the anions of strong acids, and in the presence of the hydroxyl anion the co-valent pseudo base α-pyranol (26) is formed with resultant breakdown of the aromatic structure.

It is noteworthy that pyrylium salt derivatives occur in nature as pigments in flowers, fruits and berries as glycosides. These compounds, known as anthocyanins e.g. cyanin chloride (27) have been extensively investigated by Willstatter[14], and by Robinson and Todd[15].



(27)

(28)

No representative of thiapyran (28) or salts corresponding to the pyrylium salts have been reported as yet. In view of the greater stability of sulphonium as opposed to oxonium salts we must accept that other criteria must be applied when examining a structure for aromaticity other than mere electron sextet formation.

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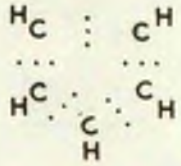
A.I.4. Anhydronium Bases.

The concept of the 'aromatic sextet', so well expounded by Armit and Robinson[12][13] led to speculation concerning the existence of aromatic types as yet unknown, and in particular to pentamethine (29), the lower analogue of benzene. Such a molecule is, of course, a radical, and it cannot form a 'sextet' from unutilised valency electrons. This, however, does not apply to the anion (30) derived from cyclopentadiene (31), which consequently should possess some aromatic stability, and in point of fact cyclopentadiene and its benzologues indene (32), fluorene (33) and 4:5-methylenephenanthrene (34) display acidity, forming sodium and potassium derivatives, this property being used in their extraction from coal tar.



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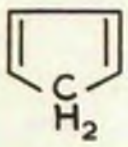

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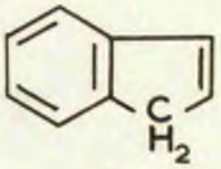

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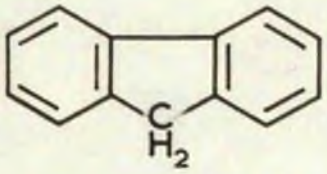

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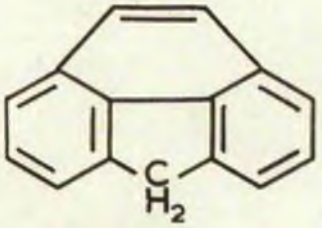
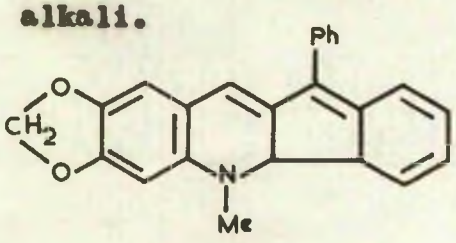


(34)

In order to investigate the possibility of the pentamethine nucleus existing in fusion with another ring system, the above authors synthesised the two highly-coloured indenoquinoline anhydro-bases (35) and (36) by decomposition of the corresponding methosulphates with alkali.



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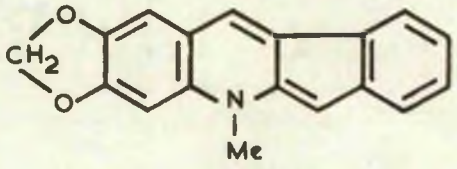

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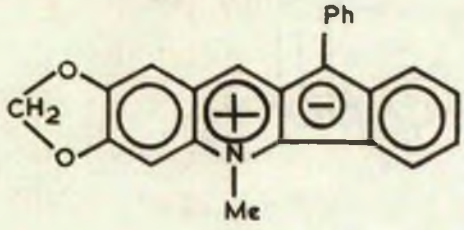

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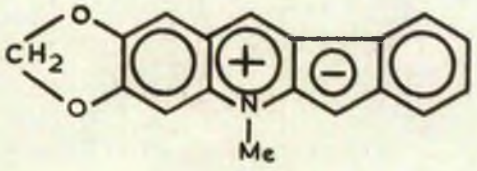
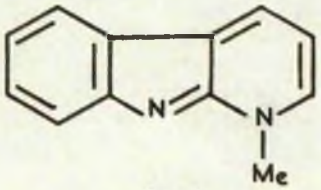


(38)

It is possible to draw up electronic arrangements in these compounds involving 'sextets' in each ring, though this would render the molecules in a dipolar form as in (37) and (38). The resultant molecule must lie somewhere in between the two extremes, as the uncharged molecule is unconjugated and would not be expected to be aromatic in the central rings, whereas, on the other hand, it is unlikely that the aromatic

stability conferred on the molecule by 'sextet' formation would be sufficient to render it fully dipolar. By analogy, it is possible to prepare anhydro bases involving the pyrrole anion, e.g., that derived from β-carboline shown in both its neutral (39) and dipolar form (40).



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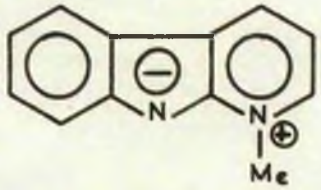
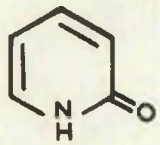


(40)

To the type of compound which existed as some mean between a neutral and dipolar form, Robinson gave the name anhydronium base. The classification includes a very wide range of substances where partial sextet formation is achieved by a redistribution of electrons, the ejaculation of an excess electron from one site in a molecule and its absorption by another. The superfluous electron need not be absorbed in 'sextet' formation; the resulting anion can be a suitable electronegative atom. Such must be the case to a greater or lesser extent with both α- and γ-(N-methyl) pyridones shown in neutral (41,43) and dipolar forms (42,44), and also α- and γ- pyrones, in neutral (45, 47) and dipolar (46, 48) forms.



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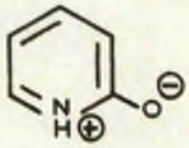

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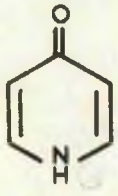

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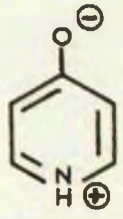

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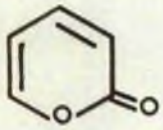

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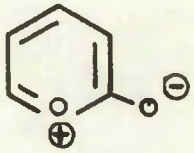

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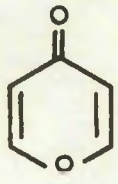

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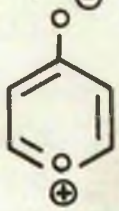


(48)

Molecules which have a potential for forming these dipolar structures would be expected to show considerable modification of the

reactivity of the oxygen function. This is observed experimentally, particularly in the case of γ-pyrone, and though there is a carbonyl group present in the uncharged form (47), carbonyl reactivity is severely suppressed by electron redistribution; exceptionally γ-pyrone reacts normally with Grignard reagents.

A.II. THE 'AROMATIC SEXTET'.

A.II.1. Introduction.

In the preceding section, the earlier standpoint of the organic chemist with regard to the theoretical aspect of the stability of aromatic compounds has been stated, and it was shown how these purely empirical concepts can be built into working hypotheses which can both account for observed phenomena and simultaneously predict the existence of unknown systems. It is the object of the ensuing discussion to develop this viewpoint further with a critical discussion of the electron sextet in carbocyclic systems; to show how the organic chemist can, by correlating both the information obtained from organic reactions and also from physical measurements such as acidity, basicity, dipole moments, absorption spectra etc., build up a framework of theory which is at one and the same time useful in both chemical investigation and as a speculative tool.

It would, however, be inconsistent at this stage to remain blind to the purely theoretical aspect of aromaticity and organic reactions which is the outcome of the wave mechanical approach to the structure of the atom. Though, of course, rigid wave mechanical formulae have been derived both for the hydrogen atom and molecule, an extension to more complex systems has proved impossible due to the complexity of the mathematical calculations involved. Two principal non-empirical approximations have been widely used as a basis for the theoretical investigation of organic chemistry; the valence bond and molecular orbital approximations developed largely by Pauling[16] and Coulson[17] respectively. Confidence in the application of either approximation may be derived from the fact that in the main both have produced the same results.

The valence bond approximation has been the object of both eulogy and condemnation, as, of the two, it approximates more closely to the ideas of the organic chemist. Thus, as a basis for theoretical calculations, an aromatic structure is considered to be a hybrid of a

number of valence bond structures, the contribution of each structure being so chosen that the energy of the hybrid is identical with the experimentally observed energy of the structure. Such valence bond structures have, of course, no existence in fact, and the resulting hybrid is not amenable to graphical representation. The hybrid has been variously termed a 'resonance' hybrid and the 'mesomeric' state the latter term being preferable as it more clearly emphasises that the resultant molecule is not in oscillation between a number of structures (c.f. Kekulé), but has a structure which is somewhere between the valence bond forms.

The molecular orbital approximation is no doubt a closer approach to the actual picture of the molecule. Wave mechanical calculations are based on the consideration that in a molecule valency electrons are distributed in molecular orbitals derived by a linear combination of atomic orbitals. The orbitals of normal covalent bonds occupy a volume extending between the two atoms which is disposed symmetrically along a line joining the centres of the two atoms. These bonds are termed σ bonds. In the case of double bonds, the second pair of valency electrons occupies an orbital above and below the σ-orbital with a node along the line of centres. These are termed π-orbitals, and in the case of conjugated double bonds more stable π-orbitals may be derived which extend throughout the conjugated system rather than between two individual atoms. Benzene represents a particular case where the cyclical conjugation permits the formation of highly symmetrical π-orbitals of extreme stability.

In the normal tetrahedral disposition of the carbon valencies, four equivalent atomic orbitals containing the valency electrons are obtained by a hybridication of the 2s, 2px, 2py and 2pz atomic orbitals. In aromatic carbon this hybridisation is confined to the first three orbitals which are disposed in a planar configuration subtending angles of 120° to each other; the 2pz orbital taking part in the π-bond formation. Thus one of the essential requirements for aromaticity in

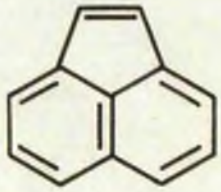
a carbocyclic system is that the annular carbon atoms should have their three σ bonds radiated in a planar configuration with angles of 120° to each other; in this connection, benzene being an example par excellence. The lowering in potential energy and consequential increase in stability which results when π-electrons become delocalised in orbitals extending over several carbon atoms is often termed delocalisation energy.

It must be emphasised that calculations in both approximations utilise non-empirically devised parameters, and as a consequence results are sometimes obtained which are at variance with experimental fact, and render the ascribing of values to these parameters a matter of extreme difficulty. In present circumstances, therefore, whereas results of wave mechanical approximations serve as a valuable adjunct, when used judiciously, in the development of aromatic chemistry, this approach will have to make great advances before it can replace the intuitive ability of the organic chemist.

One of the most notable predictions of the molecular orbital approximation, as developed by Hückel[18], is that completely conjugated planar carbocyclic poly-olefines which possess $(4n+2)$ π-electrons (where n can be 0, 1, 2, 3 etc.) will be unusually stable by virtue of possessing fully filled molecular orbitals with considerable delocalisation energy. The most notable success of Hückels Rule lies in connection with the cyclopentadienide anion (49), benzene, and the cycloheptatrienylium cation (50) (where n in the above formula is 1). The rule has frequently been applied, without formal proof, to polycyclic hydrocarbons, but

(49)

(50)



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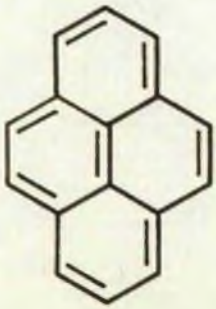

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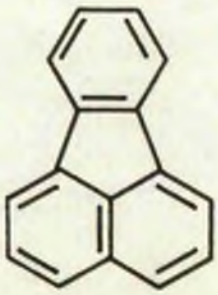
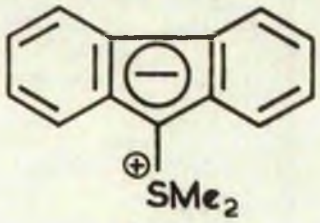


(53)

the existence of stable compounds such as acenaphthylene (51), pyrene (52), fluoranthene (53) etc., serves to safeguard against this unwarranted assumption. More recently it has been shown by molecular orbital calculations based on both real and hypothetical small ring hydrocarbons that the rule is only justified in the case of monocyclic conjugated poly-olefines[19]. It is, of course, a more general statement of the concept of the aromatic sextet, and in the ensuing discussion the particular case of the π-electron sextet will be reviewed critically.

A.II,2. The 'Aromatic Sextet': the cyclopentadienide Anion.

The cyclopentadienide anion represents the lowest member of the carbocyclic trio in which aromatic stability is associated with a delocalised system of 6π-electrons. In order to assume the aromatic state, cyclopentadiene must lose a proton, and the acidity of this compound and its benzologues has already been noted. In addition the existence of this anion as part of a fused polycylic aromatic system has been proposed in (A.I,4.) in so far as dipolar forms contribute to the structure of the highly coloured anhydro salts of Arndt and Robinson. In the main, therefore, in compounds involving this ring system in the aromatic state a greater or lesser degree of charge separation is to be expected and conversely, the association of this system with groups which promote such charge separation should lead to stable compounds.



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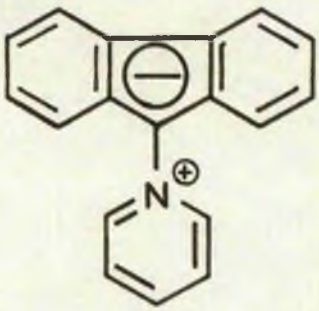

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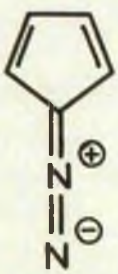

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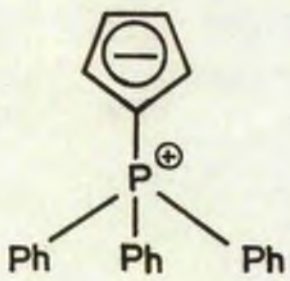
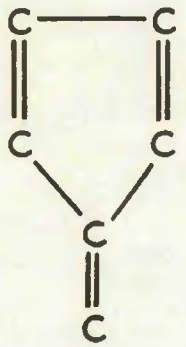


(57)

As an example of the latter statement a number of simple anhydro-salts derived from cyclopentadiene may be cited in which charge separation is doubtless nearly complete. The first example of this class of compound, though not the most satisfactory, is dimethylsulphonium - 9 - fluorenylide (54)[20] which exists as a rather unstable yellow solid. A rather better example is provided by pyridinium - 9 - fluorenylide(55)[21] a stable, salt-like solid. A more recent example is triphonylphosphonium cyclopentadienylide (57) a yellow solid[22]. The synthesis of diazocyclopentadiene, which is a red oil at room temperature, is extremely interesting, but it cannot be regarded as strictly analogous to the above compounds, in view of the possibility of structures of the type (56a) but its remarkable stability, as opposed to phenyl diazonium compounds would appear to indicate a large contribution of structures of the (56a)[23]

A.II.3. The 'Aromatic Sextet': The Fulvenes[39].

In the fulvenes there exists a series of hydrocarbons and hydrocarbon derivatives where the physical and chemical properties may be attributed to the great tendency of the cyclopentadienylide anion to be formed in a conjugated system, rather than in the environment of a strongly electron donating group such as sulphonium or quaternary ammonium. The essential feature of a fulvene is the cross conjugated system (58), electron migration from the extracyclic double bond to the ring taking place to a greater or lesser extent.



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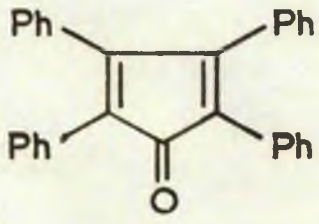
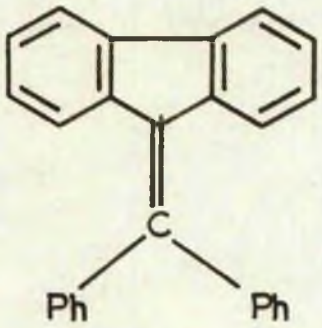


(59)

The fulvenes were first observed by Thiele[24] as the yellow to red condensation products obtained from cyclopentadiene and aldehydes or ketones, a reaction which testifies to the pronounced acidity of the former compound. The ease of condensation declines from cyclopentadiene to fluorene; presumably annelation of benzene rings absorbs the π-electrons in more stable orbitals rendering anion formation less favourable. This effect is also observed with polyarylated cyclopentadienes. An improvement in the method consists in the use of the lithio or bromo magnesyl derivative in place of cyclopentadiene itself, these compounds being readily prepared by exchange reactions with lithium phenyl and ethyl magnesium bromide respectively[25]. A second method of synthesis involves the use of fulvene ketones, available only as polyarylated derivatives, e.g. 2:3:4:5 tetraphenylcyclopentadienone (59) and a suitable Grignard reagent; the resultant tertiary alcohols are readily dehydrated[26].



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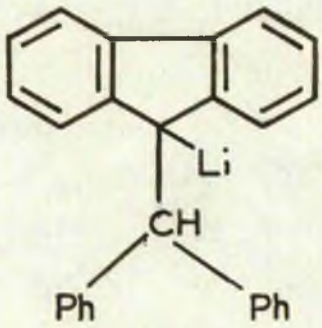

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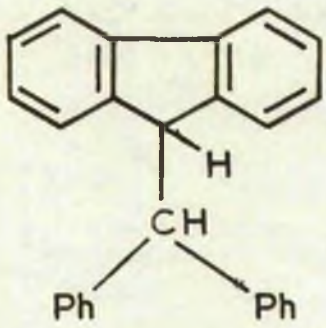

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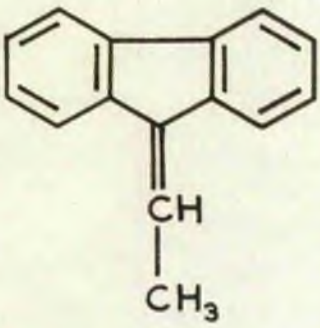

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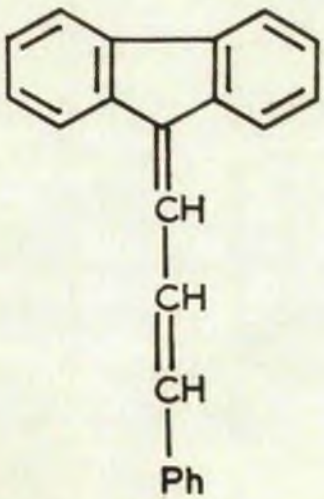

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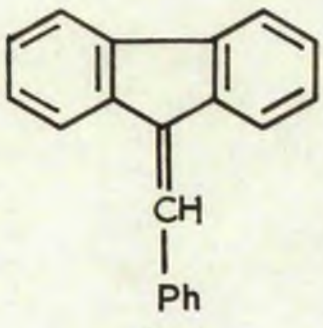

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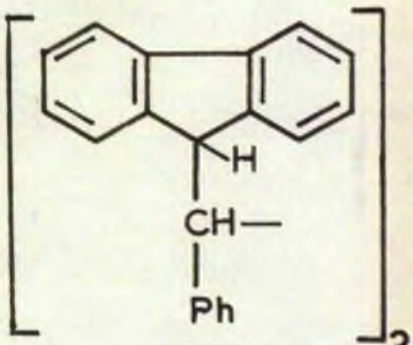


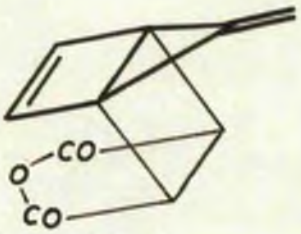
(66)

Unique reactivity of the semicyclic double bond in fulvene is to be expected on account of its polar character. Thus carbon-carbon double or triple bonds are not normally reduced by lithium aluminium hydride; exceptionally α:β-acetylenic alcohols are reduced to ethylenic derivatives. On the other hand benzhydrylidenefluorene (60) with this reagent gives a red compound which is undoubtedly the 9-lithio derivative (61) and this on hydrolysis gives 9-benzhydrylfluorene (62)[27]. By analogy of the semicyclic double bond with the carbonyl group, 6-methylated fulvenes should undergo the aldol condensation, and accordingly ethylidenefluorene (63) reacts with benzaldehyde to give cinnamylidenefluorene (64)[28]. In sodium metal reductions, one electron addition takes place at the 6 carbon site to yield an anion-radical which rapidly dimerises; benzylidenefluorene (65) yielding the dimer (66)[29]. The less highly substituted fulvenes, especially those not aryl-substituted, are prone to autoxidation and consequential polymerisation. Heating accelerates this process, and also affects the arylated derivatives, facts which emphasise that aromatic stability is a relative expression subject to considerable gradation.

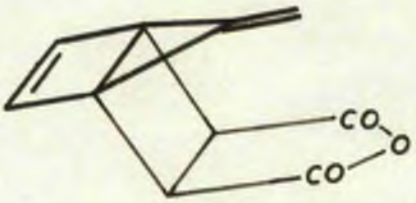
It is of supreme interest in this study that the simplest fulvene, though known for some time as an unstable yellow oil[30], has now been prepared in quantity and its physical and chemical properties studied[31] using refined techniques. In view of the localisation of a positive charge on a single carbon atom in the production of the aromatic state (67), stability in such a compound is not to be expected. At room temperature this compound becomes decolourised in a matter of hours, suffering autoxidation and polymerisation. With maleic anhydride an adduct is formed, separable into endo (68a) and exo (68b) forms. Diene reactivity, however, is exhibited by both 9-methylenefluorene (69)[32], and diphenylfulvene (70)[33], both capable of diene and dienophilic activity, and by dimethylfulvene which yields both endo and exo adducts with maleic anhydride[34]. Dienophile addition in the case of the last compounds takes place across the cyclic diene system as in (70a), a fact which once again emphasises the 'relative' aromatic stability of

the fulvenes.

(67)



(68a)



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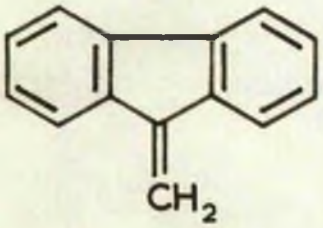

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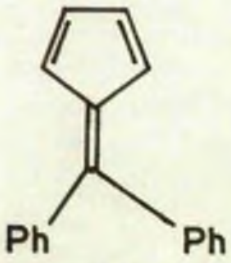

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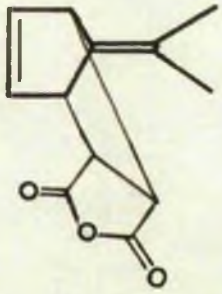
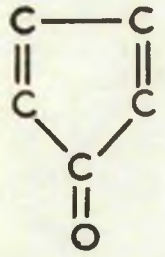


(70a)

As already noted, the colour of the fulvenes vary from yellow to red, but an examination of their visible absorption spectra does not permit of any precise interpretation, though certain trends are observable. Thus in the case of the benzylidenefluorenes, substitution in the para position of the extracyclic benzene ring generally produces a bathochromic shift, the effect being more pronounced in the case of electron-releasing than electron-attracting substituents. There might be a temptation to attribute the increasing colour intensity to a higher proportion of dipolar structures in the mesomeric state in so far as the former substituent might promote such an electron drift, but though intense colour is apparent in the anhydro-salts, particularly when a polycyclic aromatic system is involved, it must be regarded as premature at this stage to propose such an interpretation.

A more important physical property which can be related qualitatively to the dipolar tendency in fulvenes, is the dipole moment. This varies from 0.68D in the case of di-(p-chlorophenyl)-fulvene[35] to 7.85D in the case of cis-p-nitrobenzylidene-2-nitrofluorene[36]. The direction of the moment is towards the ring, and its magnitude is in accord with electron-releasing or attracting properties of the groups

involved. Of special interest is the dipole moment of fulvene itself, which, surprisingly, is as large as 1.1D. The existence of a dipole moment of such a magnitude in so simple a structure is a reflection on the great tendency of the cyclopentadienide anion to be formed.



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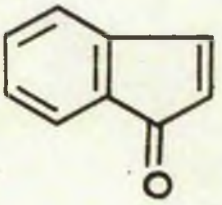

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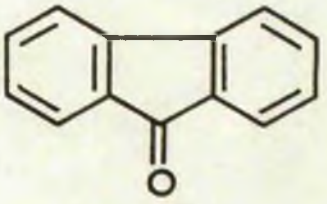


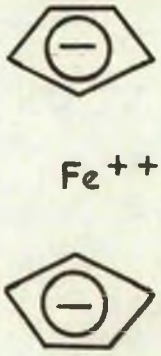
(73)

The fulvene ketones (71), which are derived from fulvenes by the replacement of the exocyclic methylene group by oxygen, are deserving of passing comment only. The outcome of the opposing electron requirements of both the cyclopentadienyl moiety and the oxygen atom appear to result in the latter drawing on the mobile electrons of the former rather than the reverse, and both chemical and physical properties confirm this. The simplest fulvene ketone is unknown, and only polyarylated derivatives, and derivatives of indone (72) and fluorenone (73) have been investigated. The infra-red carbonyl frequencies of the fulvene ketones (1710 $cm.^{-1}$ for tetraphenylcyclopentadienone; 1720 $cm.^{-1}$ for fluorenone) are much higher than those for aromatic and $\alpha:\beta$-unsaturated carbonyl compounds[37]. Dipole moment values for these compounds actually show an increase in the corresponding values of open chain ketones, but this may reflect on the polarisability rather than the polarity of the group. The chemical reactions of the fulvene ketones are not indicative of any aromatic stability or nucleophilicity in the five-membered ring, and in some respects, though not all, are analogous to ketones of the benzylidene-acetone type. In addition, tetra-arylcyclopentadienones readily behave as dienes in the Diels-Alder reaction[38].

A,II,4. The 'Aromatic Sextet': Ferrocene[40].

Two molecules of cyclopentadiene have been shown to react with one atom of a transition group metal to form compounds of extreme stability with the general formula $(C_5H_5)_2$.Metal. The original ferrocene was discovered accidentally by the interaction of ferrous (or ferric) chloride with cyclopentadienyl magnesium bromide, as in (74), a method of general application[41]. Ferrocene itself may be prepared, though in low yield, by the direct interaction of cyclopentadiene and iron at 300°[42], and the ferrocenes of iron, cobalt and chromium may be prepared by the direct interaction of metallic carbonyls and cyclopentadiene[43].

(75)



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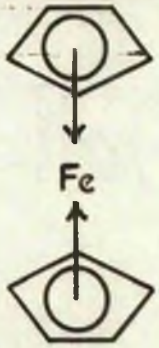

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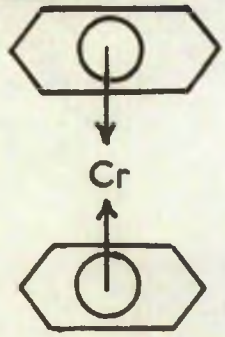

(78)

The ferrocenes have been the subject of both intense chemical and physical investigation, and only the salient features are of importance here. The pentagonal antiprism configuration (75) first adduced on suggestive evidence[44] has been confirmed by rigid X-ray analysis[45]. Infra-red spectral measurements indicate (C-H) bonds of only one type[44]. X-ray analytical data indicate an (Fe-C) bond length of 2.044Å and (C-C) bond length of 1.403 Å. The ferrocenes are diamagnetic and coloured. Observed maxima in the infra-red absorption spectrum of ferrocene[46] are retained in the ferrocinium ion[47].

Chemical properties are indicative of a covalent, non-polar compound showing well-developed aromatic character. Ferrocene, and its analogues, undergo Friedel-Crafts acylation in their five-membered rings, are unattacked by maleic anhydride, nor do they suffer catalytic reduction using Adam's platinum catalyst. They are soluble in common

$$2C_2H_5MgBr + FeCl_2 = (C_2H_5)_2Fe + MgBr_2 + MgCl_2$$

(74)

organic solvents and oxidation affects the metal rather than the organic component; ferrocene is oxidised to the ferrocinium ion, $(C_5H_5)_2Fe^+$[49]. Ferrocene is volatile is steam, and appears to be stable up to 400°. Polysubstitution experiments indicate free rotation of the two rings with respect to each other[48].

One of the original suggestions concerning the structure of ferrocene postulated the involvement of all the ring π-electrons in bonding so as to produce the configuration of the rare gas krypton around the metal[49][50]. This has been thrown open to doubt, as examples of ferrocenes are known where rare gas configuration is unattainable, for example, dicyclopentadienyltitanium dibromide, and furthermore, it would not account for the electron availability in the five-membered rings which electrophilic substitution implies. Another suggestion[51][52], which has proved more popular, is based on the molecular orbital treatment, and involves the 3d orbitals of the transition elements in the formation of two very strong covalent bonds with the cyclopentadiene rings (76).

The localisation of 6 π-electrons in each ring would result in a totally ionic structure, but such a proposition cannot be considered seriously (77), though it may exist as a limiting structure in the resonance hybrid. The pronounced covalent characteristics of the molecule coupled with the known properties of the alkali metal cyclo-pentadienides, serves to safeguard one from such a simple assumption. The above observations, however, do not hold true for dicyclopentadienyl magnesium, which cannot use any d orbitals, and must possess considerable ionic character[53].

Compounds of the 'sandwich' type are now known in which the cyclopentadiene rings of ferrocene are replaced by benzene rings. Thus the cation $(C_6H_6)_2Cr^+$ can be prepared by interaction of benzene, chromic chloride, aluminium chloride and powdered aluminium at 180°, the neutral dibenzenechromium (78) being obtained from the above by sodium dithionite reduction[54]. Structures for these compounds have been suggested which involve sharing of the π-electrons with the metal

atom, no doubt by analogy with ferrocene. The ultimate structure of all these compounds, therefore, remains obscure, and it may be that further evidence will shed some light on the problem, until which time the retention of an open mind is justified. One feature, however, is significant; though it has been possible in considering other derivatives of cyclopentadiene to invoke the formation of a delocalised system of six π-electrons to account for aromatic stability, such a concept alone used in the present context must be regarded, at best, as an over-simplification.

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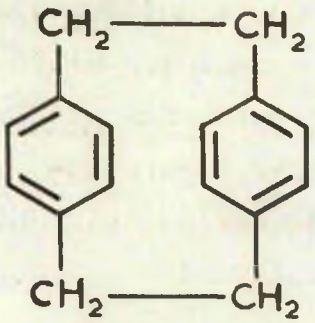
A.II.5. The 'Aromatic Sextet': Benzene.

Benzene, the first aromatic system discovered, is the foremost example of the development of aromatic character through the delocalisation of six π-electrons over a carbocyclic system. It has been thoroughly investigated and its properties are well known; it would be superfluous to discuss them here. However, one unusual aspect of its chemistry is of interest.

In (A,II,1) it was noted that one of the essential prerequisites for aromaticity was the coplanarity of all the ring carbon valencies, which should have angles of 120° to each other. It does appear, however, that some latitude is permissable in this requirement, at least in the case of benzene. Di-p-xylidene (79) a compound in which strain cannot be relieved without some distortion of the benzene rings, has been shown to be one of the products of the pyrolysis of p-xylene[55] and it has also been synthesised as one of the products of a Wurtz reaction on the corresponding bis - p:p'-dibromomethyldibenzyl[56]. X-ray crystallographic determination of the structure has shown that the two substituted carbon atoms in each of the benzene rings are displaced 0.133Å from the plane of the other four to give the resultant ring a boat-like configuration (80)[55]. Each substituted carbon atom is separated from its opposing number in the other ring by a distance of 2.83Å, and the central sections of the rings by 3.09Å (the normal Van der Waal's distance for benzene rings is 3.5Å). The aliphatic and

aromatic carbon-carbon distances are normal. Di-m-xylidene (81) has also been synthesised, and likewise shows distortion in the planarity of the benzene ring[58].



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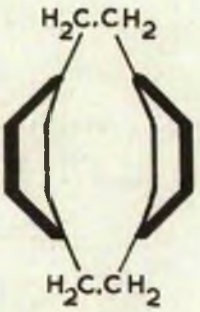

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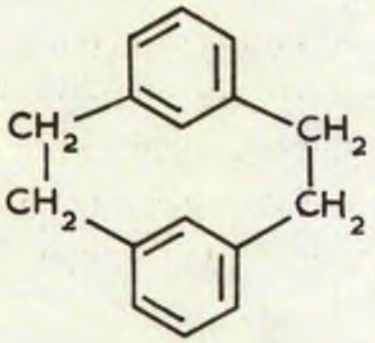
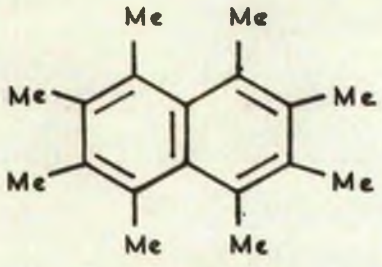


(81)

There are no accurate estimates on the loss of resonance energy, if any, which takes place in the formation of these compounds, but their mode of formation and general stability would seem to indicate that it cannot be great. The differences in infra-red and ultra-violet absorption spectra between these compounds and their open chain analogues, the dimethyldibenzyls, are small, and have been attributed in part to 'interstitial' electronic effects between the two rings[57]. Chemically, the para-linked compound has been catalytically hydrogenated to an octahydro derivative, and this is believed to be a unique example of the partial catalytic hydrogenation of a classically isolated benzene ring. The fully hydrogenated derivative, not surprisingly, is a highly overcrowded structure, and it is of interest that attempted dehydrogenation yielded only 4:4'-dimethyldibenzyl[59].



(82)

(83)

Non-planarity is also exhibited by certain polycyclic benzenoid systems. Thus in octamethylnaphtalene (82), the methyl groups, through overcrowding, are alternately displaced above and below the plane of the rings, in contrast to the fully planar hexamethylbenzene[60]. In phenanthrophenanthrene (83) or hexahelicene, molecular overcrowding at the terminal benzene rings has resulted in the molecule adopting an assymetrical spiral shape which has been resolved into optical enantiomorphs using an optically active complexing agent[61].

In conclusion, therefore, it would appear that the large resonance energy possessed by benzene is sufficient to accommodate ring buckling without any major loss in stability. In this respect benzene, and polycyclic homologues, would appear to be unique.

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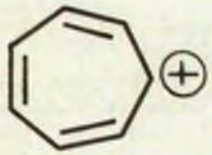
A,II,6. The 'Aromatic Sextet': The cycloHeptatrienylium Cation.

cycloHeptatriene represents the third and largest member of the carbocyclic trio in which the development of aromatic character is to be expected through the delocalisation of six π-electrons.



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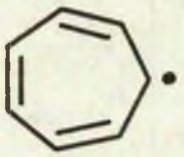

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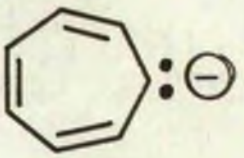
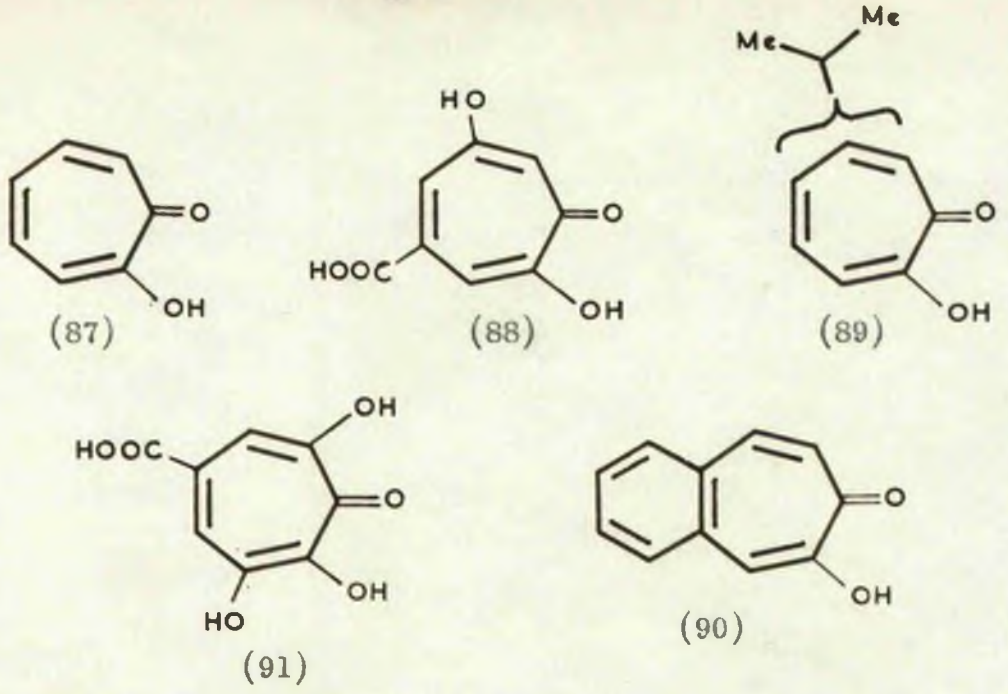


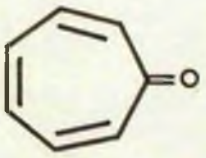
(86)

Of the three possibilities, the cycloheptatrienylium cation (84) alone would be able to fulfil the latter requirement, the radical (85) and anion (86) being invested with seven and eight π-electrons respectively. Triplet ground states have been predicted for these two entities[19]. As with the cyclopentadienide anion, the existence of this cation is only to be expected in combination with or in the vicinity of an atom or group with which it can consummate its electron requirements; in other words, in the presence of an electron sink. The stability of the resultant compound will depend on the efficiency of the electron sink as well as the tendency for the cycloheptatriene system to donate an electron.



(87) (88) (89) (90) (91)

Dewar (1945)[63] was the first to postulate the existence of a seven-membered carbocyclic aromatic system in his formulation of the tropolone system (87)[62], to account for the structure of stipitatic acid (88) a mold metabolite[64]. The structures of both these compounds have been established subsequently by synthesis[65][66] and the tropolone skeleton shown to occur widely in diverse forms, though not abundantly, in nature. Thus the three possible iso-propyltropolones (89), the thujaplicins, have been identified with the wood-destroying fungi antibiotics in the heartwood of western red cedar[67] and purpurogallin (90) present as a diglucoside in various galls[69] as well as the sodium iodate oxidation product of pyrogallol[68] has been shown to be a tropolone derivative[70]. Puberulic acid (91) is another mold metabolite[71]. Of the oxygen functions, one is enolic and the other has been termed a 'masked' carbonyl group, showing no carbonyl reactivity in the aromatic state, the carbonyl group only becoming apparent on hydrogenation of the double bonds[64]. α or β-Substitution on the tropolone nucleus gives rise to unsymmetrical tautomers, though such have never been isolated, except as the O-methylated derivatives, presumably due to high mobility of the electron system.



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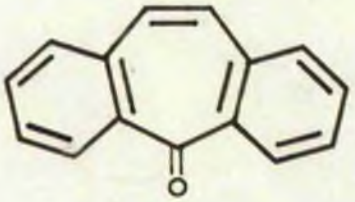

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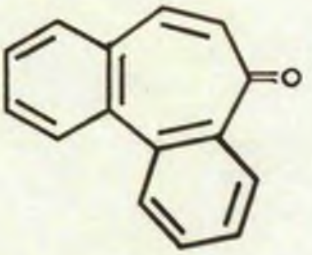
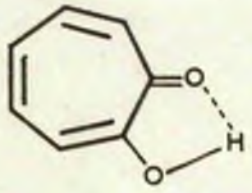
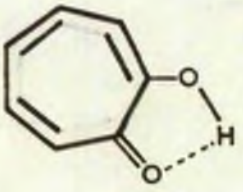


(94)

That the fundamental aromatic unit in these compounds was not tropolone was shown by the synthesis of tropone (92), a compound possessing comparable aromatic character[72]. Both compounds undergo a number of typical electrophilic substitutions such as bromination, which yields the 3-, and 3:7- derivatives in the case of tropolone, and the 2- in the case of tropone, 2-substitution being quite general in the former case. 5- Substitution is more normal in the case of tropolone, as predicted by Dewar, and this compound has the reactivity of a phenol. Nucleophilic substitution is a little more complex, and elements other than hydrogen can be displaced. Thus tropolone methyl ether yields 2-aminotropolone with ammonia, reactions of this type having been used as evidence for the concept that tropolone is a vinylogue of a carboxylic acid (see below). The simple tropolones are colourless, crystalline solids, though the benztropolones are yellow, and purpurogallin is red. Tropone is a colourless liquid, and though tropolone shows no carbonyl reactivity, tropone can form an oxime and semicarbazone under suitable conditions[62]. Of the two dibens-





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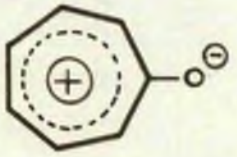

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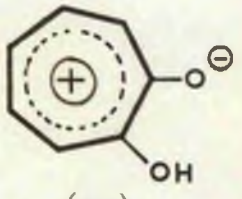
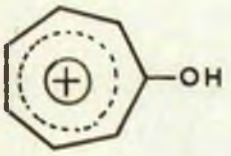


(97)

tropones (93) and (94), the former yields a 2:4-dinitrophenylhydrazone[73] and the latter has no aromatic character in the seven-membered ring[74]. Molecular non-planarity has been suggested to account for this, which contrasts with the properties of analogous compounds in the benzene series discussed in (A,II,5.).

There was originally much speculation over the fine structure of tropolone. Initial ideas overemphasised the importance of hydrogen bonding in the structure (95)[63]. On the other hand the attempt to describe tropolone as a cyclised vinylogue of a carboxylic acid broke down with the failure to find comparable aromatic stability in other analogous structures[75]. It is now generally accepted today that the aromatic kernel of these compounds is the hitherto unknown <u>cyclo</u>-heptatrienylium cation (84), and on this basis tropone has been described as <u>cyclo</u>heptratrienylium oxide (96), tropolone (97) being related to it as phenol to benzene[76]. But though such a form may contribute to the resonance hybrid, there is as yet no simple picture which adequately describes the structure of these compounds, and the fact that tropolone is more stable than either tropone or the isomeric hydroxy-tropones would seem to indicate the importance, however minor, of the 'vinylogy' concept and the hydrogen bonded forms respectively.



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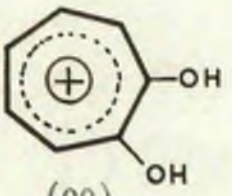

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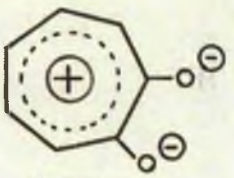

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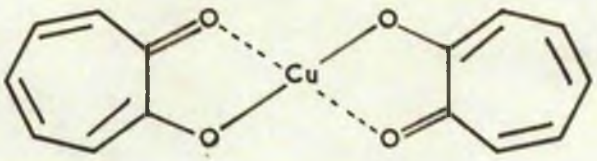
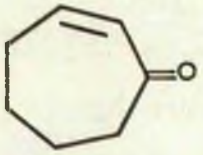


(101)

As a consequence of the fact that considerable delocalisation energy is associated with the cycloheptatrienylium cation it follows that stability should be invested in the conjugate acids (98) and (99) derived from (96) and (97). Thus tropones and tropolones are basic, the former compounds forming very stable salts with acids[72], a property less evident in the case of the latter. Tropolones, however, have amphoteric properties by virtue of the enolic hydroxyl group (100), and in line with hydroxy quinones and β-diketones this property is enhanced by juxtaposition to a carbonyl group. Thus tropolones form coloured chelate complexes with several metals, for instance, copper, with a structure of the type (101)[77]. It is of interest that ready formation of the cations (98) and (99) renders electrophilic substitution in the presence of strong acids impossible, and consequently alternative procedures have to be adopted to effect, for instance, sulphonation and nitration[62].

The dipole moment is of interest in connection with these compounds, and the values are in agreement with the assumption that the moment is enhanced by virtue of a structure of the type (96) in tropone with contributions of the type (97) in tropolone. In the latter case the dipole can be defined as being directed along a line through the centre of the ring and midway in between the two oxygen atoms. Comparison of the dipole moments of tropone (4.17D)[79] and tropolone (3.71D)[78] with cycloheptanone (3.04D)[80], however, shows that the difference is not as large as might have been expected.



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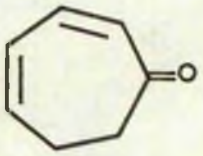

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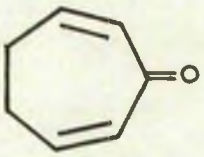

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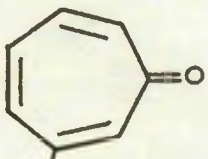
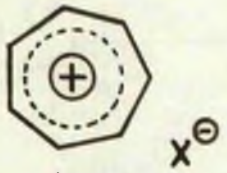


(105)

Furthermore, it has been pointed out that this neglects the effect of conjugation[81], and a better comparison would involve the dipole

moments of cycloheptenone (102), 2:4-cycloheptadiene-1-one (103) and 2:6-cycloheptadiene-1-one (104), this data being at present unavailable[62]. It is interesting to draw a comparison between tropone and γ-pyrone[47](A,I,3) and no doubt the similarity in chemical and physical properties between these two compounds has some basis in the formal structural analogy of their dipolar forms.

Infra-red spectral data shows the carbonyl frequencies to be 1638 $cm.^{-1}$, 1615 $cm.^{-1}$ and 1647 $cm.^{-1}$ in the cases of tropone[72], tropolone[82] and 3-hydroxytropone[83], as compared with 1699 $cm.^{-1}$ in the case of cycloheptanone[84]. Though the lowering of the carbonyl frequencies in all cases has been attributed to increased conjugation of this group with the ring in accord with expectation, the particularly low value in the case of tropolone is considered to be due to hydrogen bonding, and this latter point draws confirmation from the low frequency of the hydroxyl absorption. The carbon-hydrogen bond stretching frequency of 3000 $cm.^{-1}$ is in accord with aromatic nature. The ultra-violet absorption spectra of these compounds has been thoroughly investigated, but interpretation of the results is at present too obscure to help in substantiating theory.



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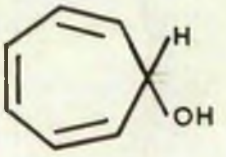

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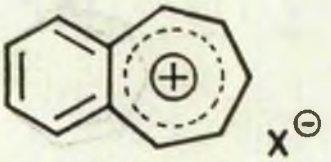

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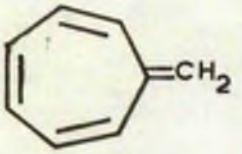

(109)

It is now possible to prepare inorganic salts (106) involving the cycloheptatrienylium or tropylium cation analogous to the alkali metal salts involving the cyclopentadienylide anion. Thus tropylium bromide though probably first prepared in 1891[85], has been recognised as the product of the action of heat on dibromocycloheptatriene[86], and it has also been prepared by an independent synthesis[87].

It is deliquescent and salt-like, existing in aqueous solution in equilibrium with its pseudo-base (107), to which form it reverts completely on basification. The benztropylium salts (108) and their corresponding pseudo-bases have also been studied[88]. In the latter case, as might be expected, the cation is associated with several pseudo-bases, and all the pseudo-base forms revert to the more stable benztropones on oxidation.

Summarising therefore, tropone, tropolone and the tropylium salts represent derivatives of an aromatic system, as testified by chemical properties such as electrophilic substitution, formation in dehydrogenation reactions etc. This is in accord with both Hückel's Rule and the concept of the aromatic sextet, which indicate that aromaticity should be invested in the cycloheptatrienylium cation. Physical evidence indicates that in tropone and tropolone there is interaction between the carbonyl group and the ring to some extent in the ground state, and chemical evidence such as lack of, or reduced carbonyl activity supports this view of the reacting state. In the case of tropolone, however, factors other than the tendency towards the formation of the tropylium cation are at least of minor importance.

The extent to which the tropylium ion is present in the normal state of the molecule is uncertain. In all the examples above, the cycloheptatriene ring is associated with an electron sink, and the tendency of this ring to resort to the cation cannot be dissociated from the ability of the associated atoms to consummate the electron transfer. In this light, the synthesis of heptafulvene (109) as a very unstable red solid is of particular interest, as it bears the same relationship to the tropylium cation as does fulvene to the cyclopentadienylide anion[89]. It is to be hoped that dipole moment measurements on this compound may be possible, as the result would provide a much more realistic expression of the ability of this system to revert to the cation than any of the previous examples.

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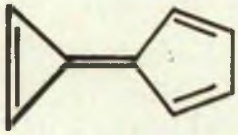
A,II,7. The 'Aromatic Sextet': Miscellaneous Polynuclear Systems.

As a consequence of the foregoing a number of potentially aromatic systems involving two linked nuclei merit consideration (fused ring systems of this type will be considered later). Huckel's Rule, in the extreme case where n=0 in (4n+2), i.e., a system of only two electrons, predicts aromatic stability in association with the cyclopropenylium cation shown in combination with other systems (110),(111) and (112) (see A,III, 2). Therefore aromatic properties would be expected of the system (111) as well as the mixed fulvalene (114) in view of the complementary electron requirements of the rings in conjugation. Conversely, aromatic properties would not be expected of the remaining systems. However a stable π-electron system has been predicted for (110) (singlet ground state)[19], and fulvalene (113), though considered to exhibit considerable bond fixation in the five-membered rings, has been predicted to possess a resonance energy of 22 k.calories per mole.,all the above being the result of M.O. calculations[90].

The three tetrabens derivatives (116), (117) and (118) corresponding to the fulvalenes (113), (114) and (115) respectively are all known, but the extensive annelation of benzene rings confers on these compounds stability and general properties which are unlikely to be characteristic of the parent systems[39]. In the case of fulvalene (113), a number of bis-indenylidenes are known,for example (119)[91]. The preparation of fluorenylidenecyclopentadiene (120) as a dark red compound has been claimed[92], though not substantiated[36]. Tetraphenylfulvene (121) has been obtained as a brilliant red solid which shows diene activity in the unsubstituted ring, forming an adduct with maleic anhydride[93]. Perchlorofulvalene (122) is now known as a medium yellow solid of no great reactivity, presumably due in part both to the heavy substitution of the molecule by halogan, and to a warping effect round the central double bond caused by steric interference between adjacent atoms of different rings[94]. The only representative of the mixed fulvalene (114) surprisingly, is the

(110)



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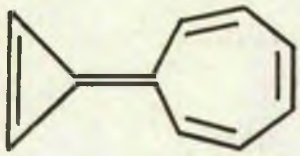

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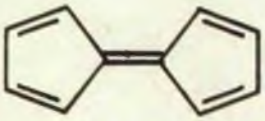

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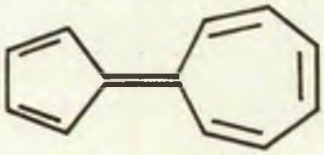

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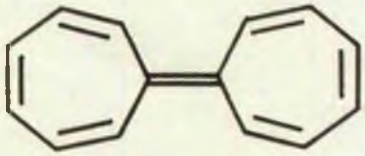

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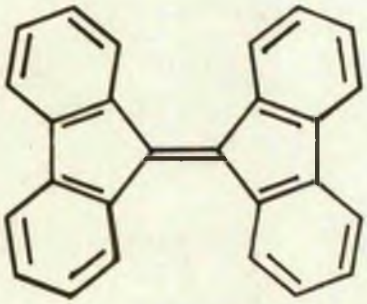

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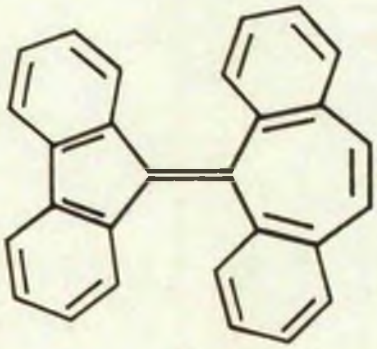

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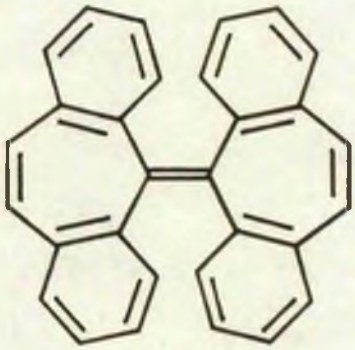

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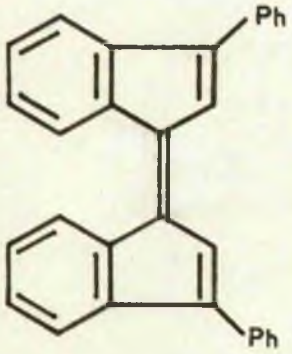

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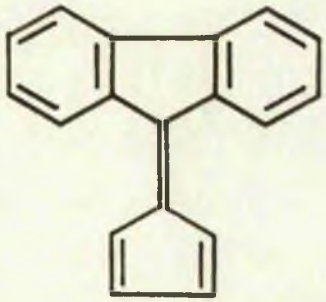

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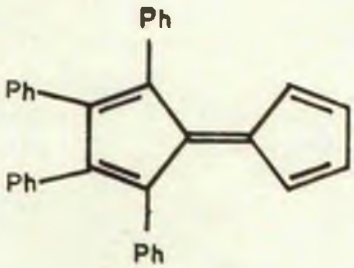

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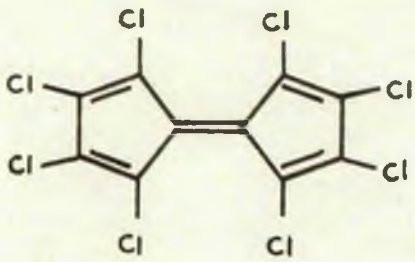

(122)

tetrabenz-derivative[95]. Finally heptafulvalene (115) has been isolated as a red solid which does not appear to possess any aromatic character, being sensitive to acids[89].

In conclusion, it does appear, in so far as regards the simple derivatives of five, six and seven membered carbocyclic systems, that the essentially organic chemists' concept of aromatic character being associated with the delocalisation of six π-electrons, is of considerable value in the interpretation of both chemical and physical properties. The ultimate implications regarding the ground state electronic structure have not been pressed, and in view of the very empirical nature of the concept, this must be deemed extremely wise; thus, though it seems reasonable in many cases to associate the chemical properties of a system in terms of a dipolar molecule, the reacting state of the molecule is inferred, and this is only a small proportion of the total molecular population. The physical data could not be interpreted otherwise, and it is clear that the energy required to maintain full charge separation would outweigh the resultant gains in resonance energy.

The relationship between the π-electron sextet concept and the physical fine structure of aromaticity is not within the province of the organic chemist to elucidate, and in common with all such concepts, it is not universally applicable, even in the limited scope discussed above. It could not, for instance, have predicted the existence of ferrocenes, nor does it satisfactorily account for their properties, and here, no doubt, a more fundamental physical concept is desirable. The organic chemist can, however, within the limits imposed by the very nature of his subject, develop ideas which,

lacking fundamental proof, can, used judiciously, be of inestimable value in the investigation of aromaticity.

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A.III. DELOCALISED π-ELECTRON SYSTEMS OTHER THAN A 'SEXTET'.

A.III.1. Introduction.

One of the criticisms which can be levelled against the concept of the 'aromatic sextet', or more appropriately against its exponents, is that it has been the subject of abuse, and its role as the monolithic foundation of all aromatic chemistry[96] seems to be unjustified. The evidence in favour of the concept, as noted in the previous section, is mainly related to the reacting state of the molecule, and does not justify any sweeping assumptions as regards the ground state. Furthermore, as indicated in (A, I, 3), aromatic sextets are frequently derived, in the heterocyclic series, from the 'spare electrons' of the valency shell of the hetero atoms, and such an arbitrary inclusion or rejection as suits the particular case seems open to rather much latitude. In the present state of our knowledge it might be more satisfactory to draw examples from the carbocyclic series, where the number of π-electrons in the system is unequivocally indicated.

The concept has been tacitly assumed to apply to polycyclic benzenoid systems, and it is true that by a process of electron sharing between rings intact electron sextets can be devised in each individual ring for the majority of such compounds, though the precise physical significance of this sharing process is not clear. There are, however, a number of examples of polycyclic aromatic systems in which no amount of ingenuity will permit the assignment of six π-electrons to each ring. Furthermore, it has been shown that Hückel's Rule is only justified in the case of monocyclic conjugated polyolefines. The extension of the sextet concept to these compounds, which display such variations in the properties of bonds and the reactivities of different sites is, at best, an unsatisfactory oversimplification.

One of the principal arguments proposed in favour of an extensive use of the π-electron sextet concept is that no alternative

system of delocalised π-electrons has been proposed to challenge it. This argument is based almost wholly on negative evidence, and is, in the opinion of the writer, fallacious. Evidence based on the non-existence of any compound can equally as well be attributed to a poor approach to its synthesis, or in extreme cases to indifferent experimental technique. Lack of aromatic character in any system does not preclude its existence as a stable polyolefine, and its identification as the latter is more conclusive evidence of a non-aromatic state than non-identification altogether.

In order that the full significance of the expression 'aromatic' character' may be appreciated when it is invoked with regard to a molecule, it is perhaps relevant to attempt a definition. Unfortunately a precise enunciation is not possible, as it refers to a diffuse set of properties which should all be possessed to a greater or lesser extent, rather than any individual property. One such property is a form of thermodynamic stability, which is precisely defined as the delocalisation or resonance energy. A less definable property, associated with the above, is chemical stability, by which is meant resistance to autoxidation and polymerisation. The ability of a molecule to undergo electrophilic and nucleophilic substitution is also of primary importance. Chemical and thermodynamic stability are the more predominant characteristics of naphthalene than ease of electrophilic or nucleophilic substitution. Contrariwise, an inverse situation obtains with regard to azulene, though all the above properties are in evidence in both hydrocarbons which are therefore said to possess 'aromatic character'. Manifestations of somewhat less importance which are also inferred by this expression include the ability to form molecular complexes which certain organic compounds whose molecules contain electron-attractive groups, e.g., picric acid or trinitrobenzene, and also with inorganic compounds whose molecules may be said to possess electron-deficient valency shells, e.g., aluminium chloride.

It is now recognised as established that in an aromatic carbocyclic system the valencies of carbon must approach the 'trigonal state', with the subsidiary prerequisites of molecular planarity and 120° valency angles which this state implies. Subject to the above conditions being fulfilled, the question arises as to whether a certain number of delocalised π-electrons is energetically favoured to the exclusion of others, or whether the choice is between selected numbers of delocalised π-electrons. Hückel's Rule is the only attempt to formalise this concept, but it makes no definite predictions about systems not embraced within the rule. It seems pertinent, therefore, to review critically the evidence, from an organic chemists' standpoint, that can be derived from a consideration of compounds which possess polyolefinic cyclical conjugated structures which do not involve six π-electrons, and to investigate whether convincing arguments can be proposed for a reappraisal of the present position.

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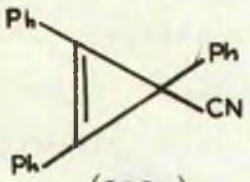
A.III.2. Two π-Electron System: the cyclopropenylium Cation.



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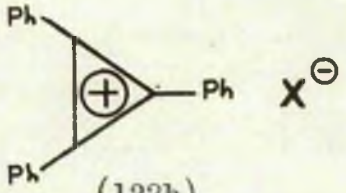

(122b)

Until only very recently 'aromatic character' associated with a carbon framework possessing less than 6 π-electron was unknown. A compound has now been described which corresponds to the lowest case embraced by Hückel's Rule where (n = 0).

Interaction of diphenylacetylene with phenyldiazoacetonitrile yields 1:2:3-triphenylcyclopropene carboxylic acid nitrile (122a). On treatment with boron trifluoride etherate, the latter is converted into what appears to be a mixture of 1:2:3-triphenylcyclopropenyl fluoborate (122b; X = BF_3) contaminated with the hydroxyfluoborate (122b; X = BF_3OH). A homogeneous compound was obtained from the above mixture by conversion to the picrate (122b; X = $C_6H_2N_3O_7$), which is bright yellow and insoluble in ether and benzene[211].

The relative stability of the sym-triphenylcyclopropenyl cation, which decomposes slowly in alcohols, is doubtless partly due to the presence of 3 phenyl groups. Nevertheless it is a unique example of the development of 'aromatic character' in association with a delocalised system of 2π-electrons, and contrasts markedly with ethylene.

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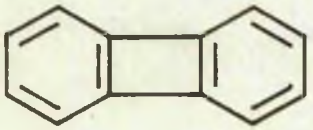
A,III,3. Four π-Electron Systems: cycloButadiene.

(123) (124) (125)

cycloButadiene (123) (unknown), as the lower homologue of benzene possessing a relatively simple structure which is amenable to calculation, has been the subject of considerable experimental and theoretical work. It occupies an anomalous position in that initial valence bond and molecular orbital treatments of it were in conflict, the former proposing a singlet ground state with a resonance energy corresponding to that pertaining in benzene, whereas the latter proposed a triplet ground state with no resonance energy[97]. The discrepancy was attributed to the fact that the molecular orbital treatment neglects resonance between Kekulé-like structures, whereas the alternative treatment neglects the contribution of polar structures. Reconciliation of the two views was suggested as a possibility if configuration interaction were permitted in the former case, and dipolar structures introduced in the latter. Molecular orbital calculations on the basis of configuration interaction (which is mathematically equivalent to a valence bond treatment involving resonance between covalent Kekulé and polar structures) indicate that cyclobutadiene possesses a small but finite resonance energy, and in accord with the original valence bond treatment, a singlet ground state. On the other hand, considering cyclobutadiene to have analogous opportunities for resonance as in benzene, the basis of the original valence bond treatment, does not seem justified and leads to a gross exaggeration of the resonance energy of the former.

(98) (99). Surprisingly the simple molecular orbital, though not the valence bond, treatment predicts stability with singlet ground states in (124) and (125) (19).



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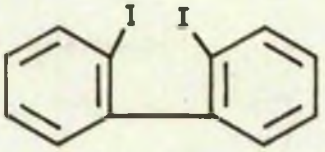

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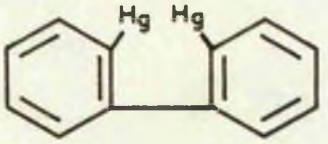
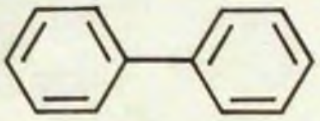


(128)

The simplest cyclobutadiene derivative known is diphenylene (126) (also known as cyclodibenzene) first obtained by Lothrop (1941) in 15 per cent yield by the pyrolysis of 2:2'-dibromo- or 2:2' di-iododiphenyl (127) with cuprous oxide (100). It has also been prepared in four per cent yield (along with tetraphenylene) by treatment of the magnesyl derivative of 2:2' dibromodiphenyl with cuprous chloride (101). Though improved technique has increased the yield in the former preparation to 21 per cent (102) diphenylene can now be prepared in 54 per cent yield by heating 2:2'-diphenylene mercury (128) (obtained from the corresponding di-lithio derivative) with silver powder at 290-300° (103). The structure of this compound, although originally the subject of doubt, (104) (105), was confirmed by electron diffraction (106) and X-ray crystallographic measurements (107).



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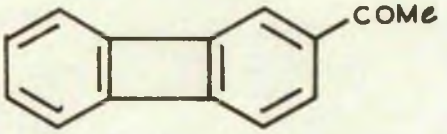

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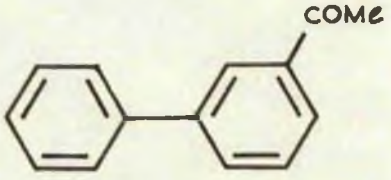

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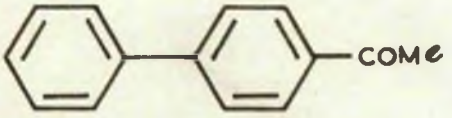
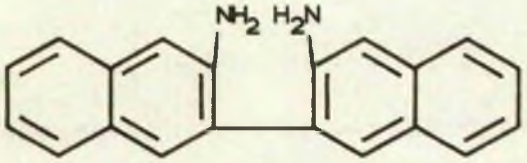


(132)

Diphenylene appears to be a relatively stable, pale yellow, crystalline solid, though reductive cleavage takes place readily in

ethanolic solution in the presence of hydrogen and Raney nickel to yield diphenyl (129). Application of the molecular orbital treatment to diphenylene has indicated that all types of substitution should take place at position 2, though, anomalously for an 'alternant' hydrocarbon, the position of greatest 'free valence' is 1 [90]. The prediction has been partly confirmed, in so far as Friedel- Crafts acylation may be regarded as a typical electrophilic substitution reaction. Thus acetylation using acetyl chloride and aluminium chloride in carbon disulphide yielded the mono-acetyl derivative (130), hydrogenolytically cleaved to a mixture identified as consisting of the 3- and 4- acetyldiphenyls (131) and (132) (1-substitution in the original compound should yield a mixture of 1- and 2- acetyldiphenyls by the same process)[102]. Remarkably, a more recent molecular orbital treatment of diphenylene predicts electrophilic substitution at position 1 and nucleophilic substitution at position 2 [108].



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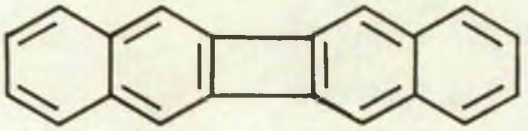

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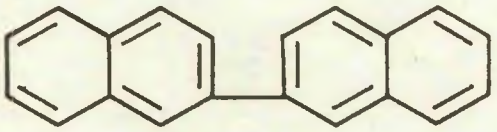

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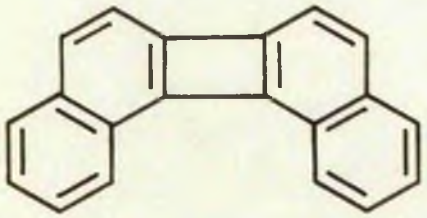

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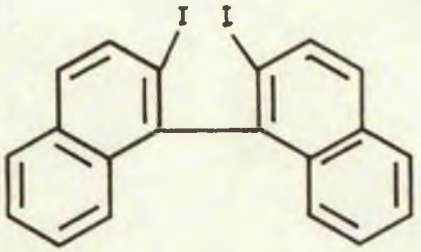
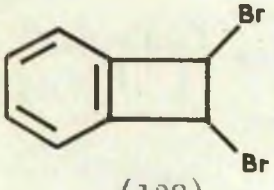


(137)

The pyrolysis of the tetrazonium salt obtained by the diazotisation of 3:3'-diamino- 2:2'-dinaphthyl (133) at a dull red heat in the presence of cuprous oxide yielded 2:3-dinaphthylene (134), a yellow solid with properties comparable to diphenylene, the structure being confirmed by hydrogenolysis in the presence of hydrogen and Raney nickel to 2:2'-dinaphthyl (135)[109]. The isomeric 1:2-dinaphthylene (136) has been prepared in low yield by the pyrolysis of 2:2'-di-iodo-1:1'-binaphthyl (137) with cuprous oxide under reduced pressure, catalytic hydrogenolysis once again yielding 2:2'-dinaphthyl (135). It is of great interest that this compound, unlike its predecessors, is orange coloured and relatively unstable, decomposing rapidly at 160°/ 3.5mm. or in boiling ethanolic solution, and more slowly at room temperature under the action of light, particularly in the U.V. region, though it appears to be quite stable in the dark. In view of the fact that the 1:2 bond shows greater 'double bond' character than the 2:3 bond in naphthalene or any bond in benzene, the properties of the latter compound must more closely approximate to the properties of cyclobutadiene than either (126) or (134)[110].



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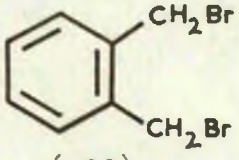

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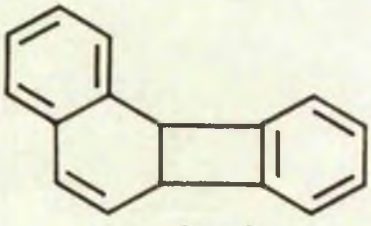
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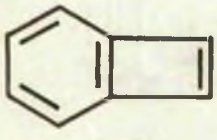
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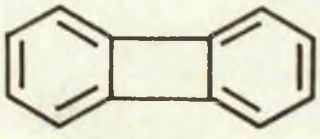

(142)

The quite stable dibromobenzocyclobutene (138) was prepared by boiling an ethanolic solution of xylylene tetrabromide (139) under reflux in the presence of sodium iodide. This compound gave no adduct

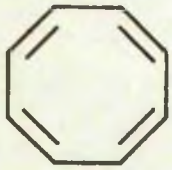
with maleic anhydride, and on oxidation with nitric acid yielded phthalic acid. However, on treatment with zinc and ethanol containing hydroquinone a high yield dihydro-2:3-benzdiphenylene (140) was obtained, subsequently dehydrogenated using N-bromsuccinimide. Doubtless in the course of this reaction benzcyclobutadiene (141) has a transitory existence, one molecule acting as a 'cyclised' styrene in a dienophilic attack on another to produce the dimer (140)[111].

A superficial glance at the diphenylene formula would suggest considerable strain in the four-membered ring, though Lothrop proposed initially that stabilisation might be achieved through the Mills-Nixon effect in the form (142). The initial estimate by Coulson of a destabilising strain energy of 100 K. calories per mole[105] must be regarded as somewhat exaggerated, and a more recent recalculation has reduced it to about 74 K. calories per mole[112]. Experimentally a value of about 59 K. calories per mole, has been obtained[113]. X-ray crystal structure analysis has indicated that the bonds joining the benzene nuclei approach single bond length[107]. The ultra-violet absorption spectra of diphenyl[114] and diphenylene[115] reveals that whereas both have maxima of comparable intensity at about 2500 Å, the latter compound has additional maxima at longer wavelength (3500 - 4000 Å) with some associated fine structure.

Both the experimental and theoretical evidence cited above would seem to overwhelmingly indicate that little, if any, aromatic character is invested in the cyclobutadiene ring system. The contention that ring strain is a major factor in the development of this condition is unacceptable, as comparable ring strain occurs in both cyclopropene and cyclobutene, both isolable compounds. It must be concluded, therefore, that cyclobutadiene itself would be a very reactive diene, which would be extremely prone to undergo intermolecular Diels-Alder addition to form polymeric products, and in this respect comparison to cyclopentadiene is relevant. In diphenylene, the length of the inter-ring bonds and the strain energy developed indicates that this molecule is probably best regarded as two benzene

nuclei (with which all the aromatic character is associated) joined in a somewhat strained fashion by two single bonds, and no molecular orbital is utilised involving the four carbon atoms of the four-membered ring for the delocalisation of four π-electrons. As an extension of the above, it must be stated that, in accord with Hückel's Rule, it does appear that a delocalised system of four π-electrons is not energetically favoured.

A,III,4. Eight π-Electron Systems: cyclo-Octatetraene.



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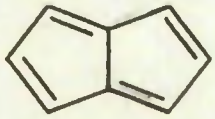
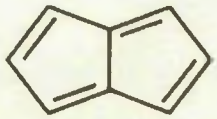


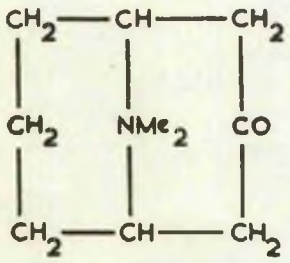


(143)

In order to investigate the potential development of aromatic character through the delocalisation of eight π-electrons, more than one system merits consideration. Thus it is pertinent to examine the properties of the pentalene (143) system in addition to the more obvious example, cyclo-octatetraene (144). In the former compound, though formally represented as possessing a dicyclic molecule, the two Kekulé forms do not permit of any double bond in the trans-annular position, on which basis there is at least no prior reason for not including it in the same category as the latter compound. In addition, one or two heterocyclic compounds will be considered in which delocalised systems of eight π-electrons have been postulated.

cyclo-Octatetraene was initially prepared by Willstätter in his classical synthesis starting with pseudo-pelletierine (145), and involving four independent elimination reactions, the final step being the distillation of the quaternary hydroxide (146) at low pressure to yield the product (144) as an orange coloured liquid. The latter was unstable to air, and resinified slowly, exhibiting a limited degree of unsaturation. Thus one molecule of bromine was

absorbed by addition to give a crystalline dibromide $C_8H_8Br_2$ whereas further bromination yielded an incompletely characterised bromo dibromide, $C_8H_7Br_3$. Structural proof lay in the uptake of four moles of hydrogen in the presence of an active platinium catalyst to yield a compound believed to be cyclo-octane, subsequently oxidised by nitric acid to suberic acid (147)[116][117].



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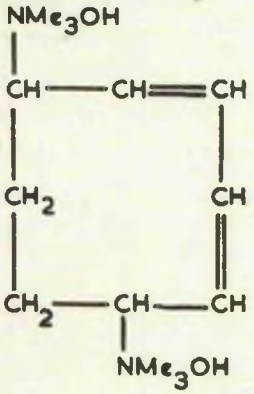

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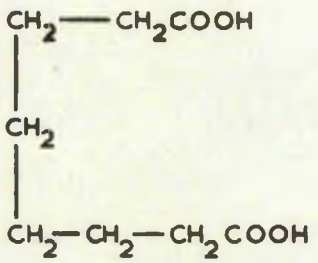


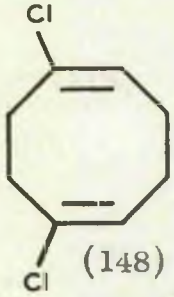
(147)

In view of the great theoretical interest in connection with cyclo-octatetraene, it was not surprising, in the lapse of time, that the work was thrown open to question some years later. The similarity in chemical, and to a lesser extent in physical properties of styrene and those recorded by Willstatter for his compound led to an attempted identification of the latter with the former[118], an idea no doubt enhanced by the fact that dehydrogenation of cyclo-octene over a chromium oxide catalyst at 300° leads to a 93 per cent yield of styrene[119]. However, no convincing evidence to establish this point was forthcoming, and the matter was finally settled in a somewhat spectacular fashion by the synthesis, as a result of German wartime research under J.W.Reppe, of what was believed to be genuine cyclo-octatetraene by the tetramerisation of acetylene under 15-20 atmospheres pressure in the presence of a catalyst (for example, nickel cyanide) and a solvent such as tetrahydrofuran[120]. The physical properties of the products from both Reppe's and Willstatter's synthesis did not show absolute correspondence, though doubtless the quantity of material available in the latter case was small. This

synthesis has now been repeated, and the product shown to be identical to that of Reppe's[121]. Furthermore, cyclo-octatetraene has been prepared from the chloroprene dimer (148) by successive dehalogenation, bromination (using N-bromsuccinimide) and dimethylamination to yield (146) identical with Willstätter's penultimate product, likewise converted to the final product[122]. Another preparation utilises tetrabromocyclo-octane (from the bromination of dehalogenated chloroprene dimer), which after treatment with dimethylamine to yield (149) is converted to cyclo-octatetraene by the usual exhaustive methylation procedure[123].

The chemical properties of cyclo-octatetraene have been exhaustively investigated, and only the salient features of its reactivity will be considered here. At the outset, it can be stated that the reactions are more in line with those of an unsaturated polyolefine than an aromatic hydrocarbon, though on account of facile rearrangement which takes place to derivatives of p-xylene (150), ethylbenzene (151) and bicyclo(4.2.0)octane (152), it is seldom that full olefinic properties manifest themselves in addition reactions. However, catalytic hydrogenation takes place in a fairly normal fashion, and in the presence of platinium and palladium catalysts four moles of hydrogen are absorbed to give cyclo-octane, though the relatively greater speed with which the first three moles are taken up permits a high yield of cyclo-octane to be obtained by interrupting the hydrogenation at a suitable stage[120][124]. Chemical methods of reduction involving lithium or sodium yield the dilithio- or disodio- derivatives respectively, which on acidification give a mixture of the two cyclo-octatrienes (153) and (154)[120], though in the former case a complex mixture including a dimer (cyclo-octadienyl-cyclo-octadiene) results[125].

Oxidation of cyclo-octatetraene can take a variety of courses depending on the reagents and conditions used. Vapour phase oxidation over vanadium, molybdenum or titanium oxides gives high yields of benzoic acid, whereas oxidation with chromium trioxide in



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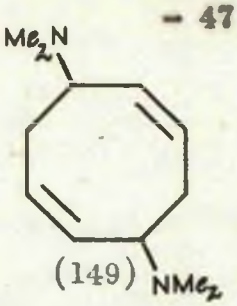

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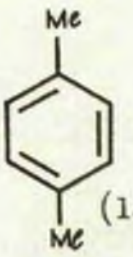

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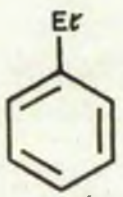

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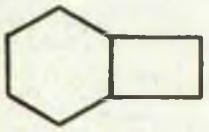
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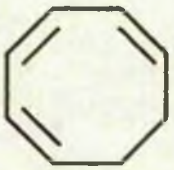
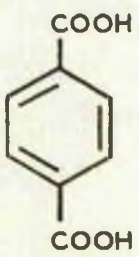

(153)


(154)

acetic acid, aqueous potassium permanganate or alkaline hydrochlorite leads to terephthalic acid (155), benzoic acid and terephthalaldehyde (156) respectively as the principal products. Phenylacetaldehyde (157) results, directly by oxidation with aqueous mercuric sulphate, and indirectly as the acid rearrangement product of the epoxide (158) formed by oxidation of cyclo-octatetraene by perbenzoic acid in chloroform[120].



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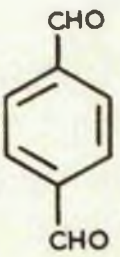

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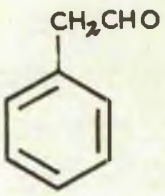

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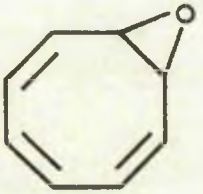

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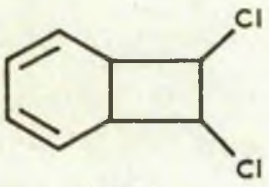

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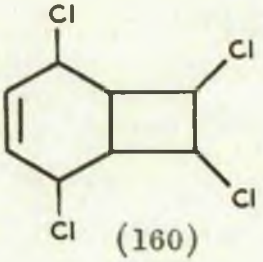

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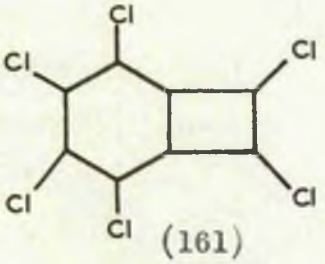

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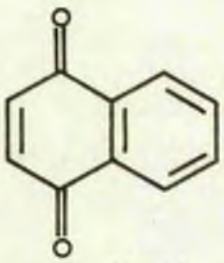

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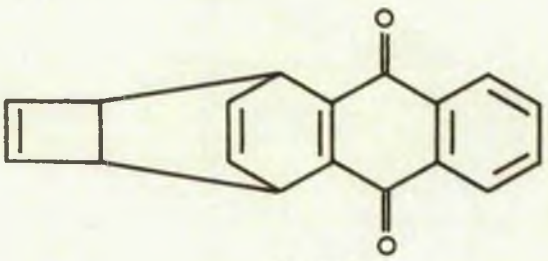

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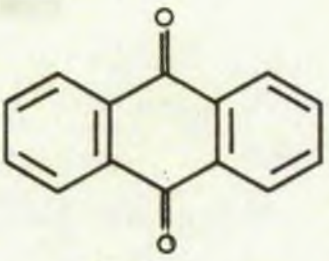
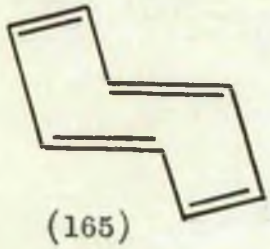


(164)

As indicated above, a feature of substitution reactions with cyclo-octatetraene is the facile rearrangement to bicyclo(4.2.0)-octatriene (158), and the partial unsaturation observed by Willstätter may be interpreted in terms of the formation of this structure. Thus, depending on reaction conditions, di-(159), tetra-(160),and hexachloro-(161) substituted derivatives can be prepared, but further chloro-substitution is impossible. As might be expected, cyclo-octatetraene shews diene reactivity with a variety of dienophiles, but once again rearrangement takes place and only one molecule of dienophile is added on. Thus the adduct with naphthaquinone (162) is believed to have the formula (163), as evidenced by the occurence of anthraquinone (164) as a pyrolysis product of the oxidised adduct, though in this as with other adducts, the presence of the cyclobutene ring or the position of the double bond have not been established unequivocally. cyclo-Octatetraene dimerises both on standing and more rapidly on heating to give a mixture of a solid and a liquid hydrocarbon,the former only in the presence of air. Though structural evidence is lacking it seems likely that dimerisation is of the Diels-Alder type (cf.cyclopentadiene)[120].

Structural investigation has confirmed the non-planarity of the cyclo-octatetraene molecule, and of the three possibilities (165),(166),and (167), the 'tub' (166) and 'crown' (167) forms have



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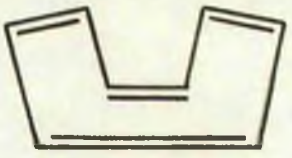

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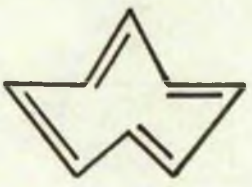
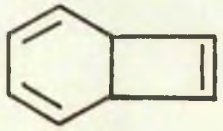


(167)

been given the most serious consideration. X-ray crystal structure analysis, which incidentally indicates a system of alternate double and single bonds, favours the 'tub' form[126],though electron diffraction measurements(which also indicate a polyolefine structure)

on cyclo-octatetraene vapour, can, apparently, be interpreted to fit both 'crown'[127] and 'tub'[128] forms. On the other hand, the infra-red and Raman spectra determined in the liquid and vapour states for both cyclo-octatetraene and its deuterated analogue are regarded as being more satisfactorily interpreted on the basis of the 'crown' form[129]. A serious objection to the latter, lies in the fact that it involves the twisting of the (C=C) double bonds by about 80°, for which there is no precedent in any other compound, normal olefinic structures involving planar double bonds. The 'tub' form is capable of adjustment so that all the (C=C$\overset{C}{\diagup}$)angles are 120°, no twisting of the double bonds being required, and on the basis of this[130] and a further electron diffraction study[131] it has been concluded that the bulk of the evidence supports this form.

Though the war-time German workers postulated that the various reaction products of cyclo-octatetraene could be accounted for if it was assumed that the compound reacted in three different forms i.e. (144), (168) and (169),



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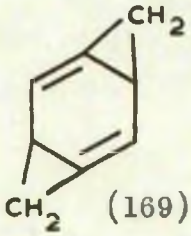

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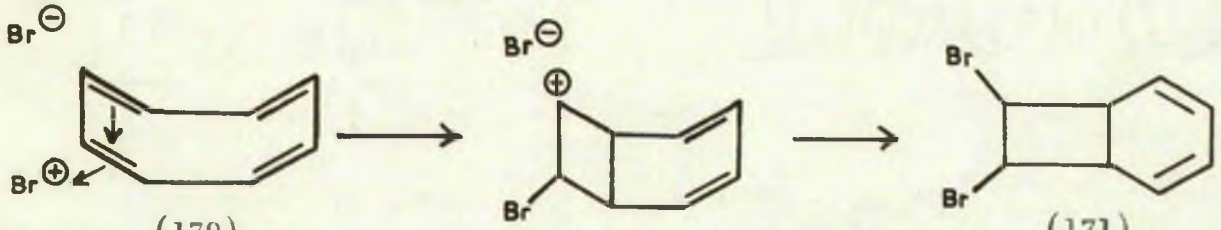
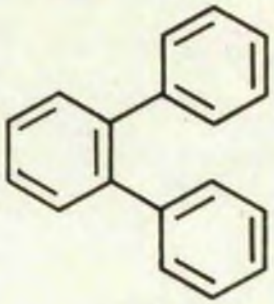


(170) (171)

such an explanation is unacceptable on a variety of grounds. It has been suggested that, assuming cyclo-octatetraene to have a 'tub' form, one could visualise the addition of bromine, for example, as a trans-annular rearrangement involving the participation of neighbouring double bonds as in the reaction scheme (170) to (171)[132]. Doubtless this scheme can be extended to embrace other reactions of cyclo-octatetraene, and transannular rearrangements have been observed for

cyclo-octane in the alicyclic series[133].

Early estimates of the resonance energy of cyclo-octatetraene from heat of combustion data, giving values of 25.8[134] and 28 K. calories[135] per mole, now appear to have been somewhat exaggerated, and more recent values of 4.5[136] and even 3 K.calories[137] per mole seem more in accord with the observed properties of the compound. The polarographic reduction of the latter at a voltage(half wave potential) of -1.5 volts is indicative of an olefinic rather than an aromatic hydrocarbon[138]. Ultra-violet absorption spectrum measurements show that whereas there is a considerable difference in the spectrographs of triphenyl (172) and triphenylene (173), this is not so in the case of tetraphenyl (174) and tetraphenylene (175); the formation of a new aromatic system by ring closure in the former case does not find



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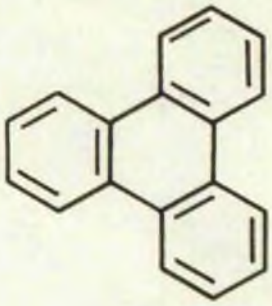

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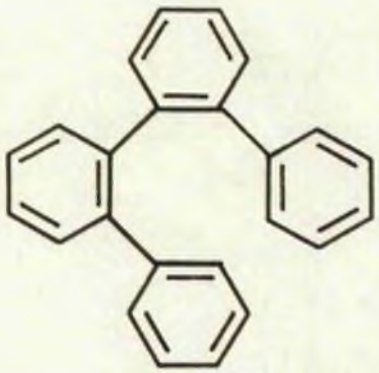

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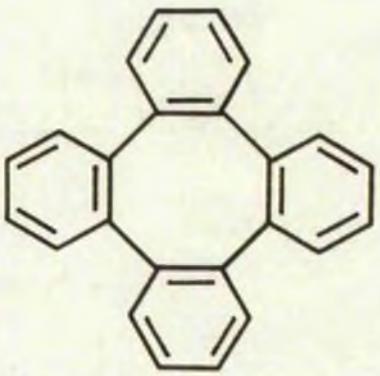

(175)

a parallel in the latter[139].

The valence bond approximation has not been of service in dealing with this compound beyond a calculation of the hypothetical

resonance energy assuming the formation of a resonance hybrid of Kekulé structure by analogy with benzene, there being abundant evidence that no such analogy exists[140]. Calculations by a non-empirical method in terms of both the valence bond and molecular orbital treatments with a view to examining the energetics of various π-electron systems indicate that the system of eight π-electrons does not show the required ground state symmetry associated with the aromatic character of benzene[99].

The adoption of a planar configuration by cyclo-octatetraene would result in ring valencies of 135° instead of 120°, and though this would lead to considerable strain, it cannot be regarded as prohibitive in respect of the formation of a resonance hybrid. That the latter does not take place must be taken as an indication that the principal cause for the lack of aromatic character in this compound is in the intrinsic incapability of eight π-electrons to become delocalised.

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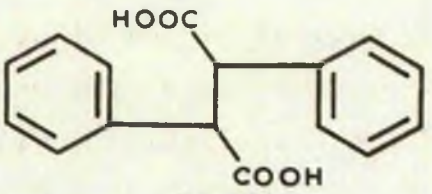
A,III,5. Eight π-Electron Systems; Pentalene.

Empirical molecular orbital and valence bond calculations using parameters derived from known benzenoid substances predicted that pentalene should possess a considerable resonance energy, though there was disagreement in the two treatments as to the identity of the ground state, and consequently it is questionable whether reliance can be placed in these predictions [141]. Craig, by an extension of the particular case of cyclobutadiene worked out non-empirically and in detail, has shown that certain criteria for the prediction of resonance energy with particular regard to the energetics of the π-electron systems apart from those obtained by analogy with benzene, are not fulfilled in pentalene, which is thus expected to show marked unsaturation and have bonds of unequal length[99]. Calculations of the π-electron densities, free valencies, bond orders and bond lengths in the case of pentalene have been made[90]. The parent system is unknown, and apart from one or two

attempts to prepare it and a mono-benz derivative, all the experimental evidence regarding pentalene has been obtained from 1:2:4:5-dibenzpentalene (181) and its derivatives.

The first authentic pentalene to be recognised was 3:6-diphenyl-1:2:4:5-dibenzpentalene (180), a dark brown solid prepared by Brand by the dehydration of the carbinol (179), in formic-acetic acid mixture, obtained by the action of phenyl magnesium bromide on



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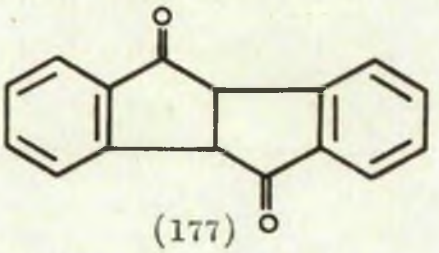

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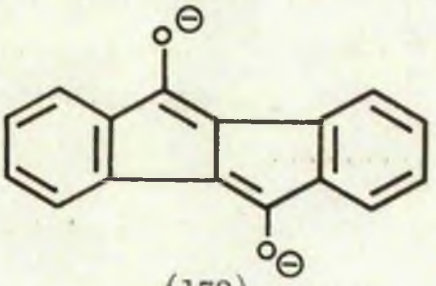

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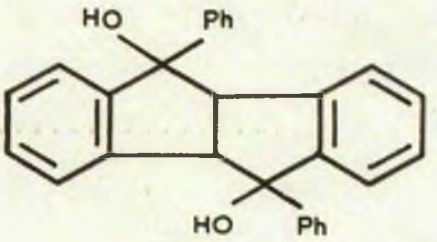

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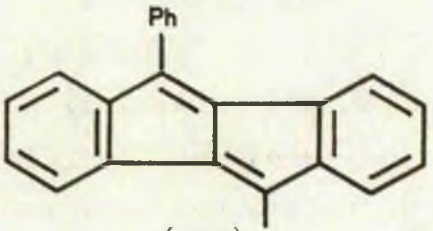

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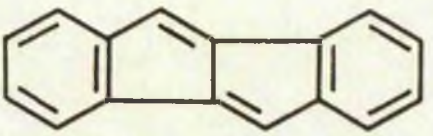
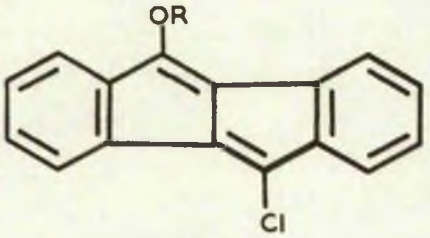

(181)

on diphenanecindandione (177)[143]. This latter compound is prepared by the action of concentrated sulphuric acid on diphenylsuccinic acid (176) at 180°[142], and dissolves in alkali to give orange-red solutions. Comparison of the latter colour with that of the dibenzpentalenes led Brand to the conclusion that a dienolic form (178) was responsible for this colour. The constitutional reason for the colour

would appear to have its origin in the conjugated double bond system lying between two benzene rings. It was therefore postulated by Brand that the parent dibenzpentalene (181) should be coloured, but a considerable volume of research by the latter worker and his collaborators failed to produce this compound[143].



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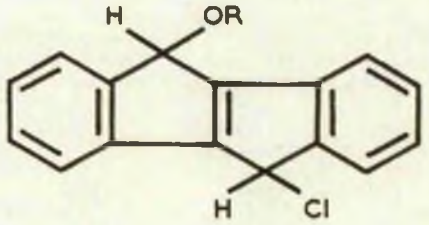

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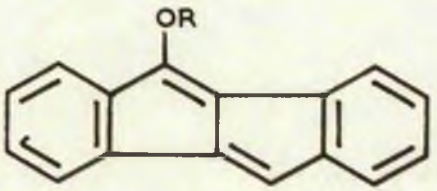

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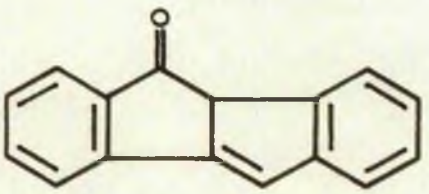

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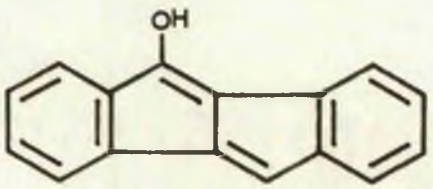
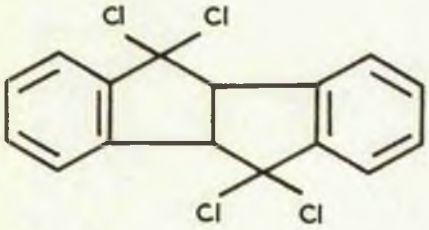


(186)

Attempts were made to synthesise the di-alkyl ether of the dienolate (178), which should possess comparable colour. However, the action of sodium alkoxide on dichlorodibenzpentalene (188)(for preparation see under) produced only the mono-alkoxy derivatives(182;R=CH_3or C_2H_5)[147]. The latter, however, could be reduced to the corresponding dihydro derivative (183) by the action of zinc and acetic acid, whereas in the case of zinc and boiling ethanol dehalogenation took place to yield (184). If the reduction was carried out using zinc

amalgam in boiling ethanol, both dehalogenation and de-etherification of the ether took place to yield what is considered to be the keto-form (185) of 9-hydroxydibenzpentalene (186)[149].



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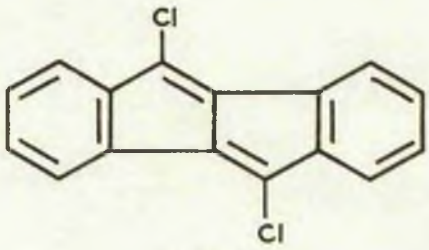

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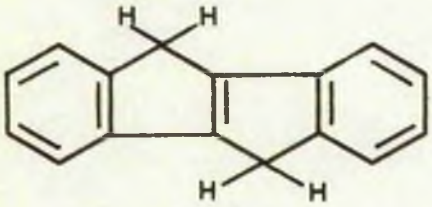

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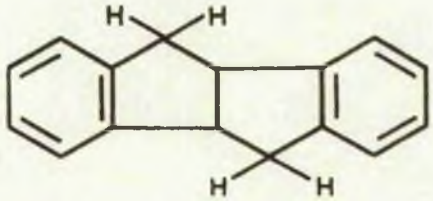

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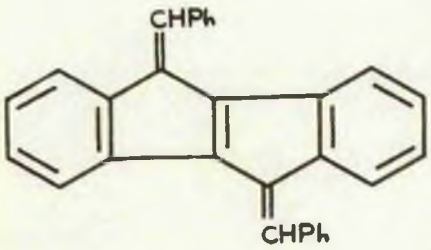

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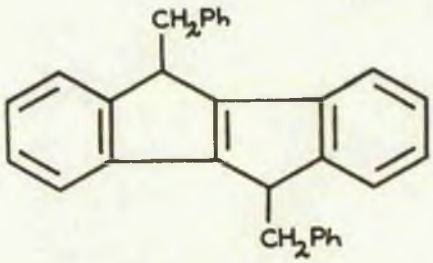
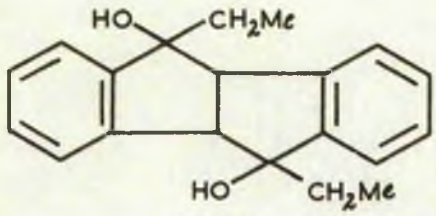


(192)

As a possible route to the parent derivative dichloro-dibenzpentalene (188) was synthesised by the action of phosphorus pentachloride on (177) which initially yields the tetrachloroderivative (187), the latter spontaneously decomposing to (188) with loss of hydrogen chloride on heating. Attempted dehalogenation of (188) using in turn tin and boiling ethanol, amyl alcohol or acetic acid only resulted in the production of the colourless dihydroderivative (189), which on further reduction by catalytic methods gave the corresponding tetrahydrodibenzpentalene (190). The dihydroderivative (189) undergoes a base-catalysed condensation with two mole-

cules of benzaldehyde to yield the vermilion red dibenzylidene - dibenzpentalene (191). The latter undergoes reduction to the dibenzyl derivative (192) using zinc and boiling acetic acid[144]. This work was later repeated and the structure of the dihydroderivative confirmed[150]. The dihydrodibenzpentalene (189) prepared above was never obtained in a completely colourless state, and this slightly coloured substance gave an intense colouration with concentrated sulphuric acid. Later work showed that a longer reaction time did yield a colourless product, and it was postulated that the coloured impurity was the hitherto unknown dibenzpentalene[149].



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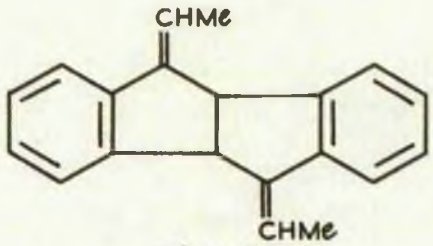

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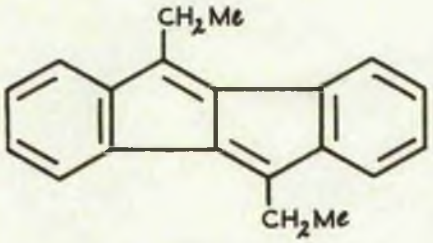

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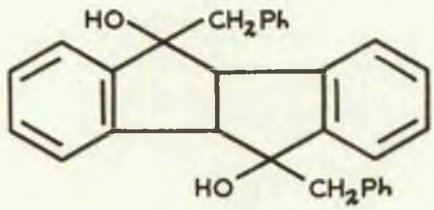

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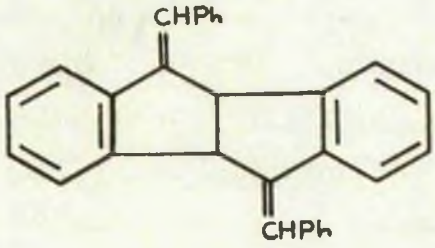

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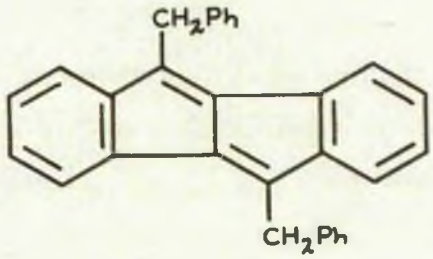
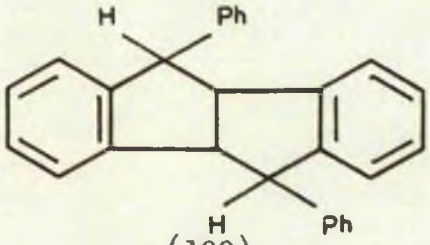


(198)

In line with the inability to isolate the dienolic form (178) is the observation that in the dehydration of the carbinol, prepared by the action of a Grignard reagent on diphensuccindandione, where possible

exocylic double bonds are formed. Thus dehydration of the carbinol (193) yields principally di-ethylidene-dibenzpentalene (194), though isomerisation to (195) is possible by treating the latter with boiling acetic acid containing a trace of sulphuric acid. However, though dehydration of the carbinol (196) yields the corresponding dibenzylidene derivative (197), attempted isomerisation by the previous method resulted in the production of a red colouration, but the pentalene (198) could not be isolated[145].



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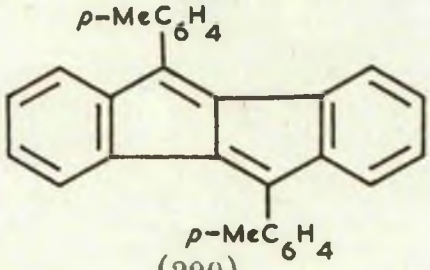

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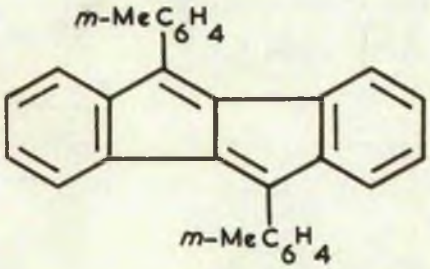

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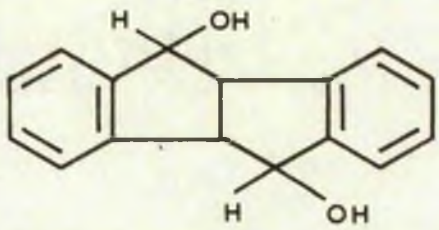

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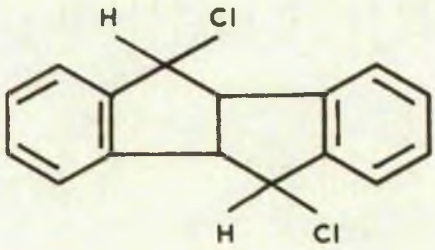
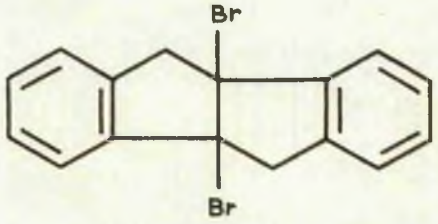


(203)

Diphenyldibenzpentalene (180) is reduced to the dihydride using zinc and boiling acetic acid, whereas reduction using sodium in boiling amyl alcohol produces the tetrahydride (199) in two stereoisomeric forms. The di-p-tolyl-derivative (200) is likewise re-

duced to two stereoisomeric forms. In the case of the di-m-tolyl-derivative (201), one form alone is produced, identical with the product of catalytic reduction of the corresponding dihydride using platinium in acetic acid. One of the two forms in each of the former cases are likewise identical with the product of catalytic reduction[146]. On the other hand, Meerwein-Pondörf reduction of the diketone (177) gives the expected di-alcohol (202), which on treatment with thionyl chloride yields the dihydro-dichloride (203). Attempts to dehydrohalogenate the latter with boiling pyridine or boiling dimethylaniline failed[148].



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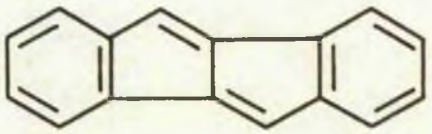
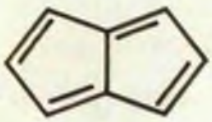


(181)

Attempted dehydrogenation of the tetrahydride (190) of Brand by Blood and Linstead (1952), both catalytically with palladised charcoal and chemically with sulphur, failed. These latter workers, however, were eventually successful in preparing the unsubstituted dibenzpentalene, the simplest pentalene ever prepared. By the careful addition of bromine to the dihydride (189) in such a manner that any of the hydrogen bromide formed was rapidly removed to prevent dehydrohalogenation and polymerisation, 3:6-dihydrodibenzpentalene - 7:8-dibromide (204) was obtained. On boiling a benzene solution of the latter compound with silver acetate, dehydrohalogenation occurred with the simultaneous formation of 1:2-4:5-dibenzpentalene (181), subsequently isolated as a bronze coloured crystalline solid. This pentalene did not undergo complex formation with picric acid or 2:4:7-trinitrofluorenone, was readily polymerised by traces of acid, formed an adduct with bromine, and was found to be insoluble in orthophosphoric acid (cf. azulenes),

though this latter property would not serve to establish lack of aromatic character as basicity would not be expected of a five-membered aromatic carbocycle[153].



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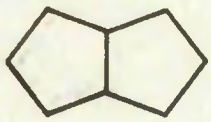

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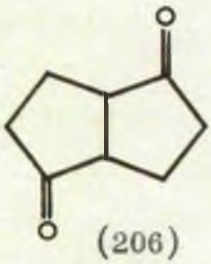

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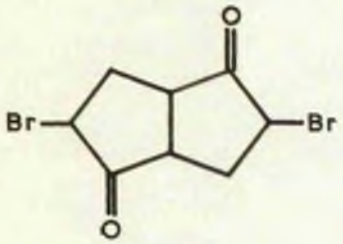

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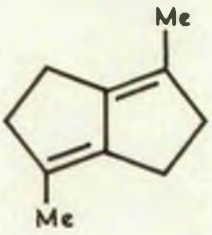

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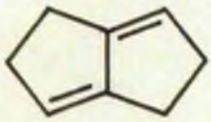
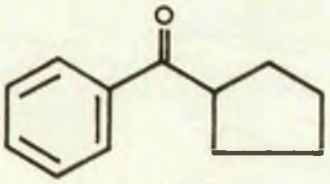


(209)

Numerous unsuccessful attempts to prepare other simple pentalenes have been described. Thus the parent pentalene (143) is not formed by treatment of cis-bicyclo(3:3:0)octane (205) under conventional dehydrogenating conditions featuring the use of platinum and selenium[151]. A number of experiments were carried out on products derived from octahydro-1:4-diketopentalene (206) in an effort to obtain similar compounds. Thus the dibromo-ketone (207), obtained by direct bromination of (206) in glacial acetic acid, could not be satisfactorily dehydrobrominated by the action of dilute alkali or silver acetate to give the unsaturated ketone. Attempts to dehydrogenate the dimethyltetrahydropentalene (208), obtained by the action of methyl magnesium iodide on (206) followed by dehydration, by means of hydrogen transfer in the presence of palladium black in boiling tetrahydrofuran, catalytic hydrogen transfer to p-nitrotoluene in the presence of palladium catalyst in boiling anisole or decalin and vapour phase dehydrogenation over palladised charcoal were all unsuccessful (tetralin is readily converted to naphthalene under similar conditions). Cata-

lytic hydrogenolysis of (206) followed by dehydration yielded the tetrahydropentalene (209) in a somewhat impure state; but bromination using N-bromosuccinimide, followed by an attempted Hofmann degradation yielded no useful material[152].



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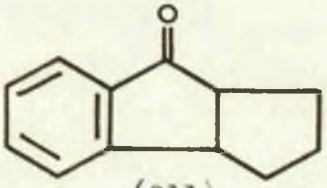

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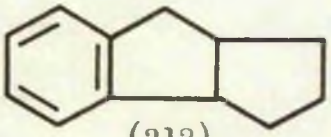

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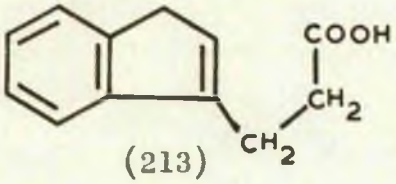

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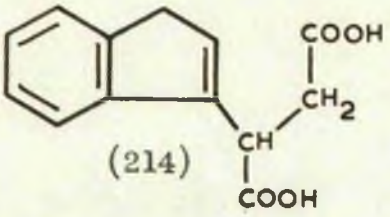

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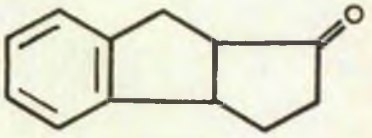

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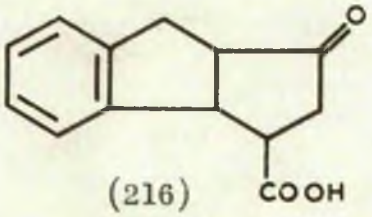

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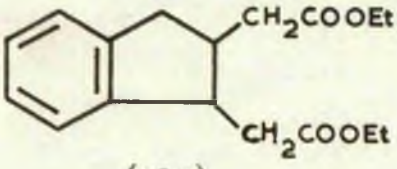

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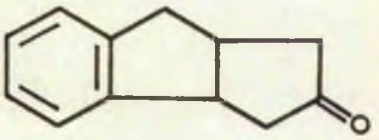
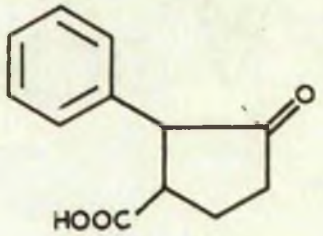


(218)

A number of perhydro-derivatives of monobenzpentalenes have been investigated with a view to the preparation of the fully unsaturated compound. The tricyclic hydrocarbon (212) can readily be prepared by the cyclo-isomerisation of 1-benzoylcyclopentane(210) followed by Clemmensen reduction of the resulting ketone (211). Attempted dehydrogenation of (212) by conventional methods(platinised and palladised charcoal, selenium) was unsuccessful, as were attempts to dehydrobrominate the monobromide, (obtained by direct bromination of (212)), using silver oxide, potassium acetate, pyridine, quinoline or ethanolic potash[154] [155].

Cyclisation of indenyl-β:3-propionic acid (212) and the half ester of indenyl-β:3-succinic acid (214), both prepared by standard procedures, yield the ketones (215)[159] and (216)[161] respectively. Though the latter with methyl magnesium iodide yielded derivatives of indefinite composition containing no oxygen, this was not possible in the case of the former, and neither could be regarded as suitable precursors of the pentalene system. Dieckmann cyclisation of (217), prepared by standard procedures from 1-indanone, yielded the ketone (218) subsequently reduced to the corresponding hydrocarbon by Clemmensen procedure. A dehydro derivative of the latter was obtained by lithium aluminium hydride reduction of the ketone (218) followed by dehydration. No useful product was obtained from either of these hydrocarbons by treatment in the vapour phase with palladised charcoal or in the liquid phase with selenium, sulphur, chloranil or a bromination-debromination procedure[160].



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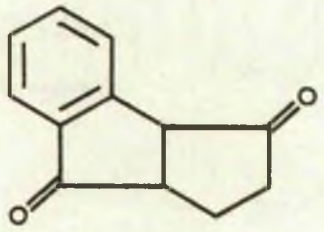

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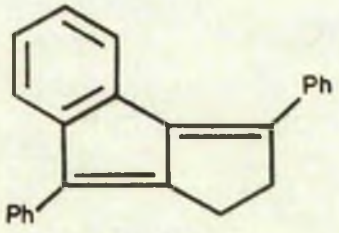

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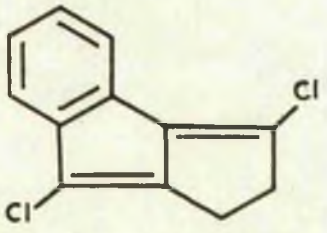
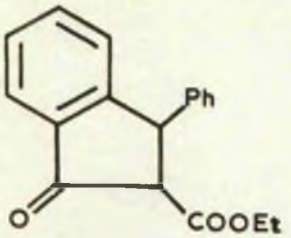


(222)

Cyclisation of 3-oxo-2-phenylcyclopentane-1-carboxylic acid (219) yielded the diketone (220), subsequently treated with two moles of phenyl magnesium bromide and dehydrated to give 4:5-dihydro-3:6-diphenylbenzopentalene (221). Attempts at dehydrogenation, including catalytic and transfer methods, and the use of chloranil, ethylene

and platinous chloride, lead tetra-acetate and selenium dioxide were all unsuccessful. The action of phosphorous pentachloride on the diketone (220) gave the corresponding chlorodiene. Bromination by N-bromsuccinimide followed by attempted dehydrobromination failed to yield the corresponding dichloropentalene(222)[157].



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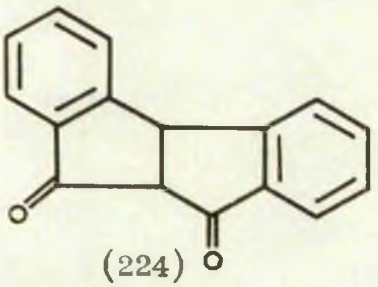

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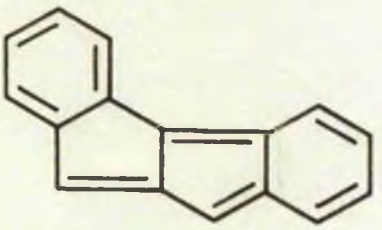

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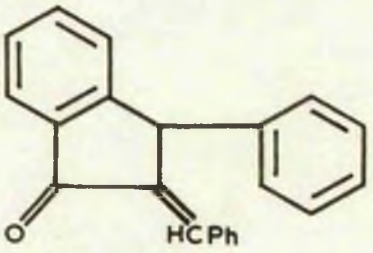

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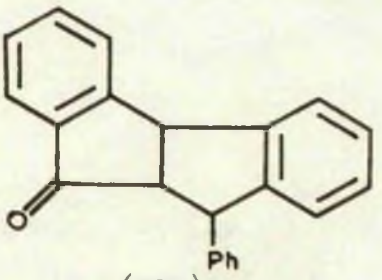


(227)

Finally attempts made to prepare 1:2-5:6-dibenzpentalene (225), the isomer of (181), or a simple derivative thereof have failed. Cyclisation of ethyl 1-oxo-3-phenylindane-2-carboxylate(223) gave the diketone (224), the latter being reduced by Clemmensen's procedure to the corresponding hydrocarbon, which, however did not submit to dehydrogenation under the action of palladised charcoal in boiling β-methylnaphthalene, tetrachloro-o-benzoquinone in benzene,or chloranil in boiling benzene. Reduction of (224) with lithium aluminium hydride yielded two stereoisomeric carbinols which could not be dehydrated. Only one mole of methyl magnesium iodide reacted with (224), and the resulting carbinol dehydrated to what is believed to be the methylene derivative. 3:4:7:8-Tetrahydro-3-oxo-4-phenyl-1:2-5:6-dibenzopentalene (227) was prepared by cyclising 2-benzylidene-3-phenylindan-1-one (226), but a series of analogous dehydrogenation experiments failed to produce the corresponding pen-

talene[158].

Once again the experimental evidence overwhelmingly indicates the lack of aromatic character in the system discussed. Pentalenes, either fused to benzene rings or otherwise, are not amenable to formation by the standard methods of catalytic and chemical dehydrogenation which produce naphthalenes and azulenes. The hydroxypentalenes show no tendency to enolise and do not give O-alkyl derivatives, the only evidence for the formation of enolones being colour development shown by the corresponding diketones in alkali. The alkylidene-dihydro-pentalenes are quite stable, and the benzylidene derivatives are incapable of isomerisation. All the known pentalenes are readily hydrogenated. In particular, the simplest representative, 1:2-4:5-dibenzpentalene, is a highly reactive compound, being readily azonised, and polymerised in the presence of acid.

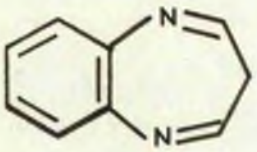
No definite conclusions can be reached regarding the possible isolability of the parent pentalene or its monobenz-derivative, though doubtless they will be reactive and olefinic in character. Many of the dehydrogenation methods used, however, would scarcely be expected to yield an olefinic substance, and in this context it is relevent to note that the failure of Brand to isolate dibenzpentalene must, at least in part, be attributed to the use of acid in many of his dehydrogenative procedures. The pentalene molecule fits all the basic requirements for the development of aromatic character, and it must be concluded that some criterion or criteria, possibly associated with the energetics of the eight π-electron system, are unfulfilled in this case.

.....

A.III.6. Eight π-Electron Systems: Heterocyclic Examples.

It is of interest that in contrast to the carbocyclic series, aromatic character has been associated with a delocalised

system of eight π- electrons over a monocyclic structure in certain heterocyclic compounds. An early example lies in the benzdiazepines (228) the first representative of which was prepared by Thiele and Steinmig as a coloured salt (230), yielding a colourless base (231), by the condensation of acetylacetone and o-phenylenediamine under



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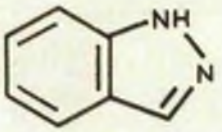

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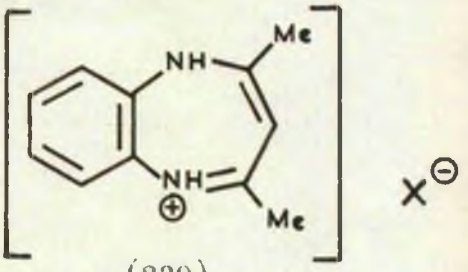

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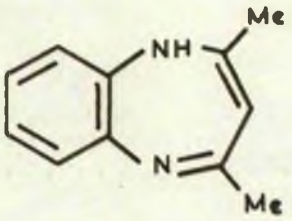

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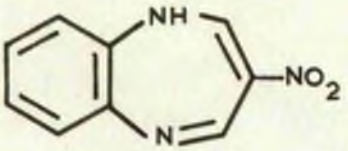

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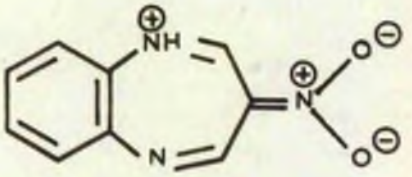
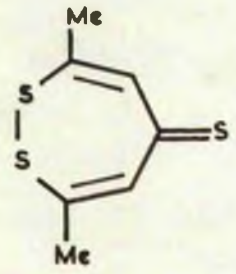


(233)

acidic conditions[162]. These compounds may be regarded as the cyclic vinylogues of the benz-imidazoles (229),and though they show considerable differences in properties from the latter, it seems reasonable to assign eight π- electrons to the mobile electron system of the seven-membered ring. In particular the benzdiazpine (232) prepared from the condensation of nitromalondialdehyde and o-phenylenediamine appears to be unusually stable; its melting point being above 360°. It is insoluble in most solvents; exceptionally it dissolves in nitrobenzene and reversibly in concentrated sulphuric acid. The compound has a somewhat low basicity, judged from its precipitation from sulphuric acid on dilution; and infra-red absorption spectral data has confirmed the existence of a high degree of polarisation. In view of the strong tendency for the nitro-group to withdraw electrons from the ring to give a form

such as (233), the properties of this diazepine cannot be regarded as typical[163].



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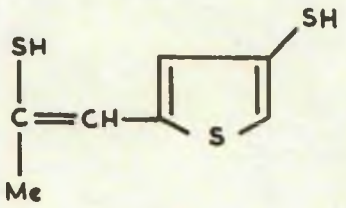

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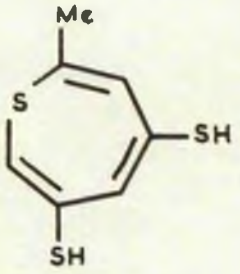
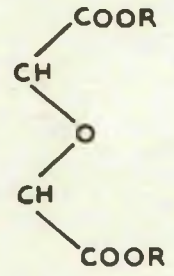


(236)

Contemporaneously with the above, Arndt suggested that the dimercaptan, prepared by the rearrangement of the cyclic disulphide (234) in alkali, and originally considered a thiophen derivative, i.e.(235), on the basis of a similarity in chemical properties, might in fact be a derivative of the unknown hexathiophen, i.e. (236). By regarding this compound simultaneously as the vinylogue of thiophen and the thia-analogue of cyclo-octatetraene, once again the possibility arises of a delocalised system of eight π-electrons[164][165]. Preliminary physical evidence has indicated that the assignment of structure (236) to the dimercaptan is correct[166].

A number of compounds have now been synthesised whose structures involve an unsaturated seven membered ring including one hetero atom. Thus the products of the base-catalysed condensation between o-phthalaldehyde on the one hand, and diglycollic ester (237), N-methylaminodiacetic ester (238; R' = CH_3) or thiodiglycollic ester (239) on the other hand are benzoxa- (240)[172][173], benzaza- (241)[168][169] or the benzthiatropylidenes (242)[170][171] respectively. The free acids (241,242; R = H) of the latter two compounds appear to be somewhat unstable, particularly so in the case of benzthiatropylidene, which resisted isolation as a stable entity on this account, though this property does not obtain in the esters

($R=CH_3, C_2H_5, C_6H_5$), and these alone have been used for the chemical investigations described. However, in the case of benzoxatropylidene, both the free acid and its corresponding esters are stable. All the



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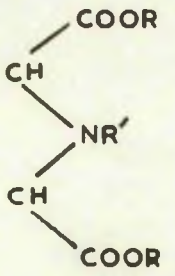

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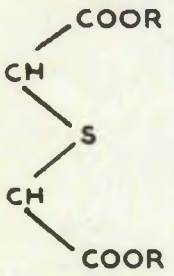

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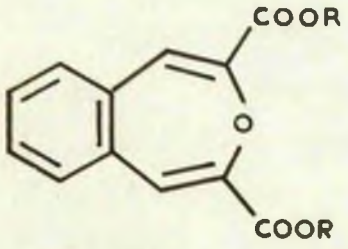

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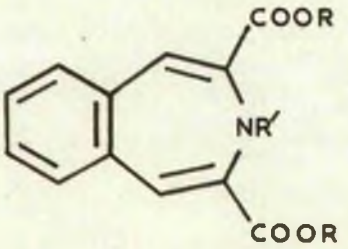

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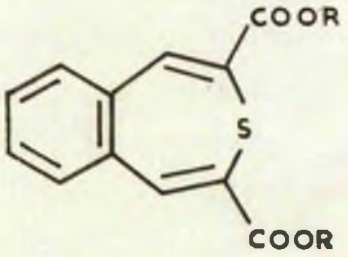


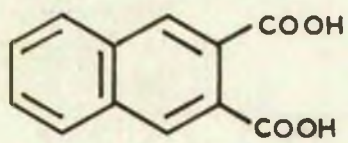
(242)

above compounds are coloured crystalline solids, varying from (241) which is orange-red, (242) which is orange-yellow, and finally (240) which is pale yellow.

In this series of heterocycles the order of reactivity and stability observed for lower analogues is not adhered to, and these properties show both an increase and decrease respectively in passing from the oxa- to thia-derivative, with azatropylidene acting as a mean between the latter two. Both the oxa- and aza- derivatives dissolve reversibly in cold and even warm concentrated sulphuric acid without decomposition, though some alteration takes place to the latter derivative over a period of some days. Thus the N-phenylbenzazatropylidene (241; $R' = C_6H_5$) is not recoverable from its solution, yielding a compound of unknown structure still containing nitrogen, whereas under similar conditions the N-methylbenzazatropylidene (241; $R' = CH_3$)produces what is considered to be 1-oxal-3-hydroxyindane-2-carboxylic acid (244), subsequently converted to the known

indene-2-carboxylic acid (245)[174]. The thia-derivative is likewise reversibly soluble in cold concentrated acid, but on heating its acid solution it is rapidly converted into naphthalene - dicarboxylic acid (243). The oxa- derivative alone is completely inert to the action of alkali, though the aza- derivative is not soluble in, and consequently unaffected by, cold alkali solutions. On warming it appears to split out the nitrogen function from its molecule. The thia- derivative, by contrast, is rapidly converted to the alkali salt of (243) under similar conditions even in the cold.

Diazomethane or methyl iodide both fail to react with either oxa- or aza- tropylidene, though thiatropylidene adds up to two moles of the former reagent to yield what is presumably a pyrazoline derivative (246). The oxa- derivative is unaffected by



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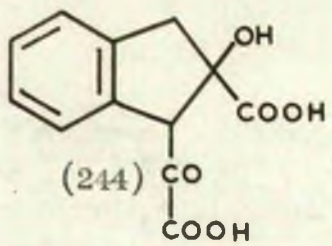

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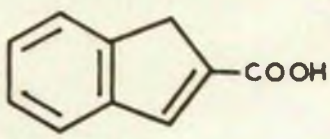

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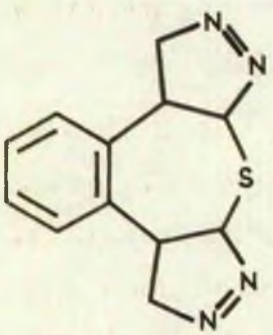

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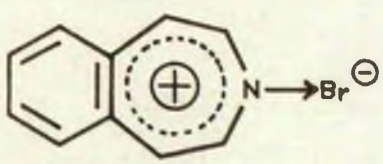

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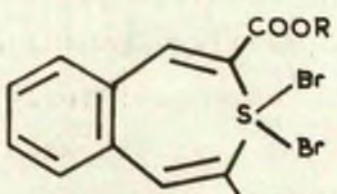

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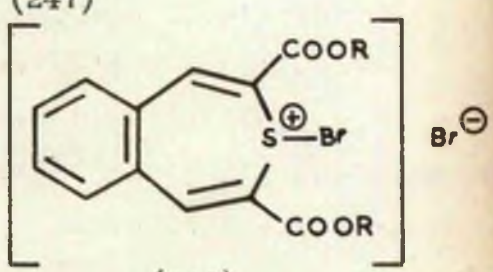

(249)

alkaline potassium permanganate which oxidises the aza- derivative to phthalic acid. Bromine likewise does not attack the former compound, though in the case of the latter it appears to displace the N-methyl group with the concomitant generation of methyl bromide and formation of an N-bromo derivative. Such a reaction may find

justification in the considerably greater electronegativity of the bromine atom permitting forms of the type (247) in accord with the known basicity of the ring structure. A mole of bromine is added on by the thia- derivative under similar circumstances, though the addition appears to take place at the sulphur atom rather than at a double bond, and structures (248) and (249) have been proposed for the bromo-adduct. Catalytic reduction of the oxa derivative in the presence of freshly reduced platinium black, and of the aza- derivative in the presence of palladium on barium sulphate results in the uptake of two moles of hydrogen in each case, the latter tetrahydro-adduct reacting with methyl iodide to produce a quaternary salt in contrast to the unsaturated compound. The benzthiatropylidene derivative yields a crystalline compound with mercuric chloride.

It is premature at this stage, in view of the qualitative nature of the chemical evidence available, to make any definite decision regarding the electronic fine structure of these compounds, and in this context physical evidence would be desirable. Thus X-ray structural analysis would indicate the planarity or otherwise of the ring, and whether the respective bond lengths were in accord with those expected of a conjugated aromatic system. It is unfortunate that in all the examples of these systems examined, the benzologues alone were available, as these undoubtedly possess a degree of stability and other concomitant properties which cannot be extended absolutely to the parent structure. However, the lack of olefinic activity displayed by these compounds towards reagents such as diazomethane and bromine definitely indicates a measure of π-electron delocalisation in the seven-membered ring, and this in particular appears to manifest itself in the cation as evidenced by reversible solubility in concentrated acids.

Whether these tropylidenes are regarded as having the same electronic structure as that obtaining in the tropylium cation or as the aza-analogues of cyclo-octatetraenes or even the vinylogues

of the five-membered heterocyclic compounds, it cannot be said that any one of the above comparisons satisfactorily accounts for the occurence of aromatic character in these compounds. Though the assignment of π-electrons cannot be made unequivocally, as in the case of the carbocyclic series, it does seem reasonable to associate eight π-electrons with the delocalised π-orbitals of the ring on account of both the inertness of the hetero atoms towards reactions which utilise the spare 'p' or 'd' (in the case of sulphur) electrons in σ-bond formation, and the fact that if these 'p' or 'd' electrons are localised on the hetero atom they effectively block the ring conjugation. Nevertheless any analogy drawn between these hetero-systems and cyclo-octatetraene with which they are iso-electronic, must be considered ill-founded in view of the latter's olefinic character, and properties such as basicity seem to find a parallel in the seven-membered aromatic carbocyclic series.

In conclusion, therefore, it appears that whereas some rationalisation of the experimental data and theoretical observations of the properties of various delocalised π-electron systems may be made in the case of polyolefinic carbocycles, extension of this rationalisation to the heterocyclic series cannot be made in the present state of knowledge.

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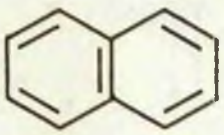
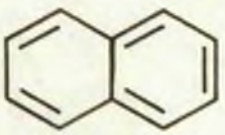
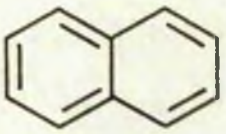
A.III.7. Ten π-Electron System: Azulene.



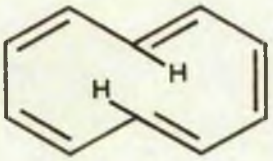
(251a)



(251b)



(251c)



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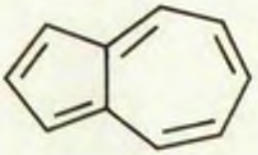
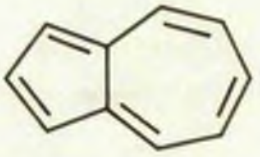


(252a)



(252b)

The cyclic vinylogue of cyclo-octatetraene is the unknown hydrocarbon cyclodecapentaene (250), and it is of some interest that this

hydrocarbon, by virtue of its possessing ten π-electrons, should exhibit aromatic character by application of Hückel's Rule. Another circumstance must be taken into consideration here, however. A scale drawing of the molecule will reveal that, in assigning angles of 120^0 to all the valencies, two of the hydrogen atoms are disposed towards the centre of the ring and will manifest considerable steric interference with respect to one another. The strain involved when this molecule adopts a planar state would in all probability be disproportionate with regard to any concomitant resonance energy which might develop as a result. Accordingly, it is likely to exist in a puckered conformation; with alternate single and double bonds round the ring. Therefore even though such a hydrocarbon were to be successfully synthesised, it is unlikely that it would yield any information concerning the potential delocalisability of ten π-electrons.

In the absence of a satisfactory monocyclic representative for examination, the two dicyclic hydrocarbons naphthalene (251) and azulene(252) both iso-electronic with cyclodecapentaene, represent the closest approximations available. In the case of both these compounds aplanarity through the steric interference of the centrally disposed hydrogen atoms has been obviated by uniting two transannular carbon atoms by a common bond. In so far as Kekulé forms (251b) and (251c) may be regarded as contributing to the resonance hybrid, it might appear that naphthalene could be regarded as a derivative of the unknown cyclodecapentaene. Unfortunately, there is abundant physical and chemical evidence that the Kekulé form (251a) plays a major role, and furthermore the properties of this hydrocarbon must be considered as more satisfactorily accounted for by treating its resonance hybrid as in the main formed from the 'fusion' of two benzene rings. Whereas naphthalene, therefore, shows a very considerable development of aromatic character and has a highly delocalised π-electron system, the electronic fine structure must be interpreted in alignment with benzene and not cyclodecapentaene.

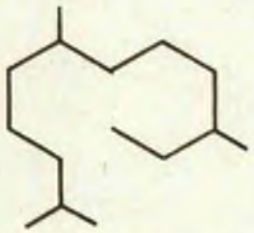
In azulene, on the other hand, the situation is not so well defined. None of the Kekulé forms (252 a. and b.) permit of transannular double bond in view of the unsymmetrical constitution of the rings, and there is as yet no physical evidence as to the length of this bond. The hydrocarbon, however, shows considerable development of aromatic character,

and has a delocalisation energy of the order of two thirds that of its isomer, naphthalene. The results of chemical and physical investigations, which will be enumerated subsequently, indicate that the electronic fine structure of azulene admits of no simple description, and is as yet open to speculation.

Azulenes have been known for over five hundred years in so far as they have been identified with the blue colour which develops as a result of distillation, treatment with acids or oxidising media etc., of certain essential oils. Systematic investigation of these compounds was made possible only after the discovery by Sherndal(1915) that they were reversibly soluble in strong acid, which consequently facilitated separation from the other compounds of the essential oils[175]. In addition, use was made of the ability of azulenes, in common with other aromatic hydrocarbons, to form complexes with sym-trinitrobenzene, picric acid etc., in their isolation. The method of isolation and purification was considerably improved by Plattner and St.Pfau, using chromatography on activated alumina, which simultaneously purified and decomposed the crude azulene complexes[177]. The relationship of azulenes to the sesquiterpenes was recognised by the occurence of the former along with substituted naphthalene derivatives on dehydrogenation of the latter. As a result of this, and oxidative experiments on azulenes and their partially hydrogenated derivatives, Ruzicka(1926) concluded that azulene must contain a hitherto unknown bicyclic ring system not involving a six-membered aromatic ring[176]. Finally, Plattner and St.Pfau(1936) in their classical structural determination and synthesis showed the structure of the parent system azulene to be (252)[177][178].

The relationship between naphthalene and azulene is particularly well exhibited in their formation in analogous dehydrogenation reactions on their appropriate essential oil precursors. Thus the open chain sesquiterpene skeleton (253) can yield on a hypothetical ring closure precursors of the cadinene (254) and eudesmol (255)

type which on dehydrogenation give cadalene (256) and eudalene (257) respectively. Analogously the same open chain sesquiterpene leads



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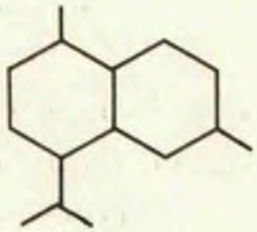

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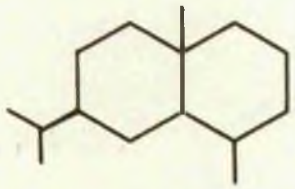

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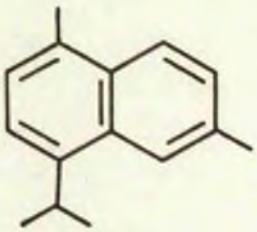

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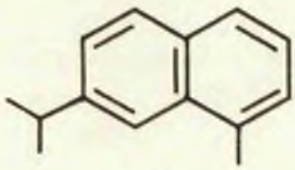

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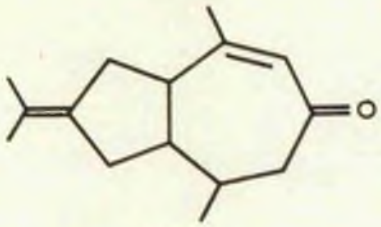

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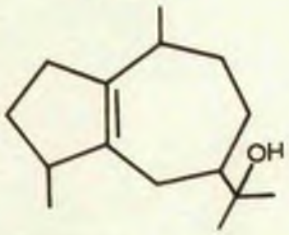

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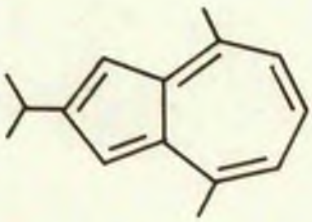

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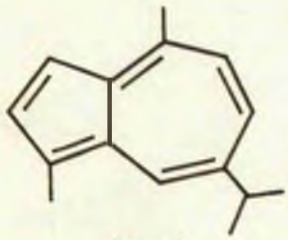

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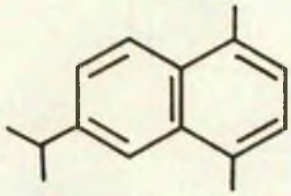

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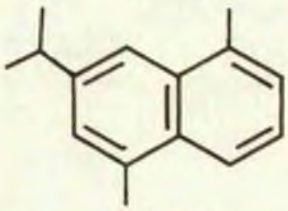

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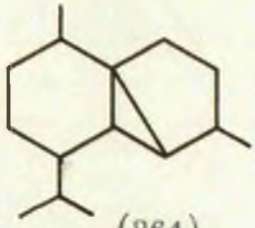
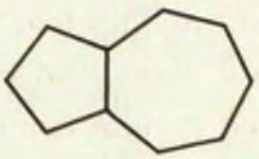


(264)

to precursors such as vetivone (258) and guaiol (259) as two possible modes of ring closure, subsequently yielding vetivazulene (260) and guaisulene (261). The relationship is further demonstrated by the fact that in addition to the corresponding azulenes, guaiol (259) yielded 6-isopropyl-1:4-dimethylnaphthalene (262), and vetivone (258), 7-isopropyl-1:5-dimethylnaphthalene (263) on reduction with hydrogen iodide and red phosphorus followed by dehydrogenation using sulphur[177].

On the other hand ledene (264) gave cadalene (256) and guaiazulene (261) on sulphur dehydrogenation[179]. In addition, a small amount of decahydroazulene has been shown to be present after catalytic reduction of naphthalene or tetralin under pressure and at 370° in the presence of molybdenum trisulphide[180], whereas the conversion of azulene to naphthalene and guaiazulene (261) to a naphthalene derivative in the vapour phase at 300° over a period of two days has been demonstrated[181].



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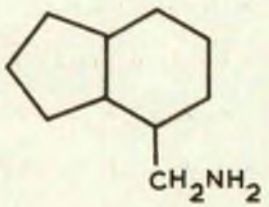
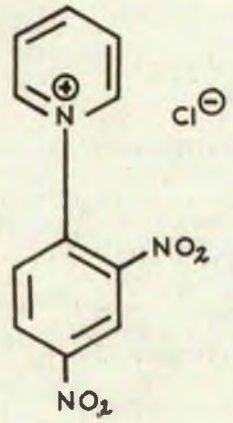


(266)

A vast volume of work has been conducted on the synthesis of azulenes, and the majority of procedures involve the formation of the appropriate 0:3:5 - bicyclodecane skeleton (265) in a varying degree of unsaturation followed by an ultimate dehydrogenation step. This skeleton has been obtained variously from 9 : 10 -octalin, by the ring expansion of indanes using diazoacetic ester[182], by the Demjanov ring expansion of appropriate hydrindanylmethylamine (266)[183], and by ring expansion utilising the addition of diazomethane to the double bond or the carbonyl group in indane[184] or hydrindanone[185] respectively. A seven-membered ring has been fused on an appropriate cyclopentane derivative[186], and a five-membered ring on to cyclo-heptanone[187] by the standard procedures of alicyclic chemistry. The methods of dehydrogenation vary from the use of sulphur at 200-220° selenium at 280° and platinium or palladium on charcoal above 300°. In common with selenium dehydrogenations generally, azulenic products often show side-chain migration; and though this is true of the catalytic methods to a lesser extent, as the latter can be used as a continuous operation in the gas phase, they have tended to be more popular[188].



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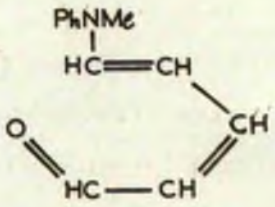

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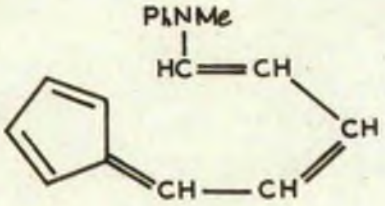

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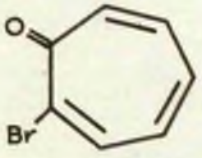

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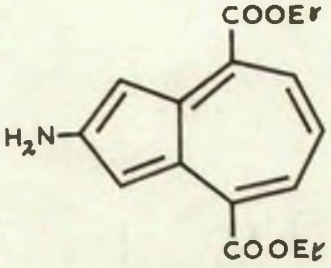
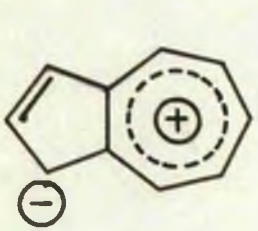


(271)

Exceptionally, a new azulene synthesis has been developed which dispenses with the dehydrogenation step. Thus 4-mono- and 4 : 8- disubstituted azulenes may be prepared from the fulvene (269), readily acquired from cyclopentadiene and glutacondialdehyde (268), at about 250° in vacuo, and yields of up to 73% have been reported. Glutacondialdehyde (268) is conveniently obtained by hetero- ring cleavage of 2 : 4 - dinitrophenylpyridinium chloride (267) in the presence of N-methylaniline[189]. In addition, the base-catalysed condensation of cyanoacetic ester and 2 - bromo-tropone (270) produces directly I : 3- diethyldicarbethoxy - 2 - aminoazulene (271) which yields either the I : 3 dicarboxylic ester or the 2 - amino derivative by deamination or decarboxylation respectively, and this method holds promise as a route to the hitherto inaccessible 2 - substituted azulenes[190]. In the case of azulene itself the preferred method still involves dehydrogenation, and optimum conditions have been described for gas phase catalytic methods where yields of over 30% are obtained from decahydroazulene and of over 60% in the case of a starting material with a hydroxyl group or a double bond in the five-membered ring[191].



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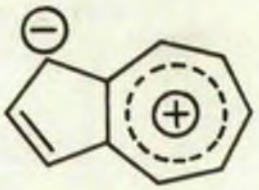
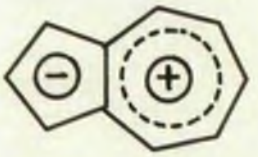


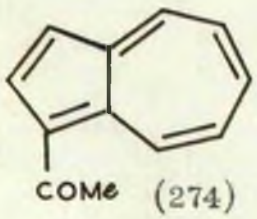


(273)

Perusal of the above suffices to show that azulene has a stability concomitant with that expected of a benzenoid hydrocarbon, and in contradistinction to the previously described pentalene and cyclo-octatetraene. This stability finds quantitative expression in a resonance energy of 46 K.cals/mole, from heat of combustion data[192], compared to 77 K.cals/mole for naphthalene. With regard to the electronic fine structure of azulene, the suggestion has already been proposed of a bridged cyclodecapentaene. Another possibility arises. It has already been indicated, in so far as reacting states are concerned, that considerable delocalisation energy is associated with the cyclopentadienylide anion and the cycloheptatrienylium cation. Fusion of these moieties might be expected to yield a molecule of corresponding delocalisation energy in that the electron requirements of the individual rings, in the terms of the 'aromatic sextet' hypothesis, are mutually consummated. This argument derives further appeal in that it would account for the lack of aromatic character in both pentalene and heptalene, where electron requirements of the individual rings are in opposition and mutual consummation impossible. Dipolar forms of the type (272), or more generally (273) are presumably envisaged.

The first suggestion that a dipolar structure was involved in the reacting state of the molecule was made by Anderson and his co-workers(1953)[193]. This proposal was greatly extended by Stafford and Reid(1954) who considered that the azulene molecule must be considerably polarised in the ground state, and that a close parallel existed between the latter and the anhydro salts. As a consequence

it was postulated that azulene was best represented as a hybrid between the normal Kekule form and those of the type (272a) and (272b)[194][195]. It is questionable, however, if the potential energy of a structure in which an electron is forced against a potential gradient would not be disproportionately large than the resonance energy developed as a result. Furthermore, a considerable dipole moment is to be expected if this hypothesis is correct, and the experimentally determined value of 1 ± 0.05 Debye units[196] indicates ground state polarisation of a very low order. It is pertinent in this connection to note that, in spite of the electron migratory complementary tendencies of both rings, the dipole moment is only of the order of that observed for fulvene itself, and this gives corroboration for the representation of azulene as a cyclised fulvene. The portrayal of the azulene molecule as a highly polarised structure would seem to be unacceptable, though the existence of a finite dipole moment gives cogency to the argument that such a form makes a minor contribution to the resonance hybrid. There is, on the other hand, abundant evidence that a dipolar structure accounts very well for the reacting state of the molecule.



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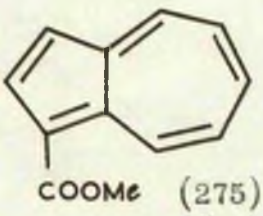

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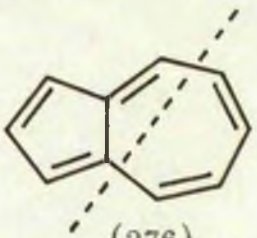

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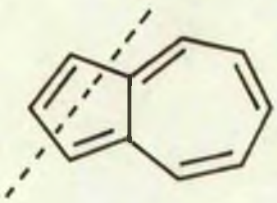

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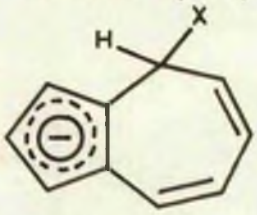

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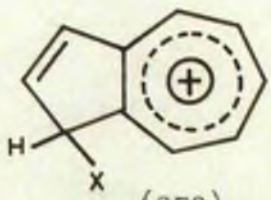


(279)

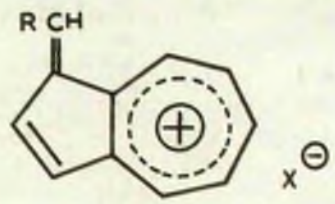
In so far as reversible proton addition to a molecule may be regarded as a very pure form of electrophilic substitution, azulene, in having an unusually high basicity for an aromatic hydrocarbon, exhibits considerable tendencies for such substitution. By a consid-

eration involving the L.C.A.O. molecular orbital approximation of the resonance energies of all the potential azulenium cations, Heilbronner and Simonetta(1952) concluded that proton addition should take place preferentially at positions 1(or 3)[197]. Anderson and his co-workers (1953) showed that 1 - acetylazulene (274) was the product of the Friedel-Crafts acylation of azulene involving acetyl chloride and stannic chloride. The mono-acetyl derivative was converted to the corresponding acid by sodium hypoiodite oxidation, the methyl ester of which proved identical with methyl 1-azulcate (275) synthesised by an unequivocal procedure. Nitration, involving cupric nitrate in acetic acid, and diazonium coupling with benzene diazonium chloride effected substitution in the same position; as shown by the conversion of both to N-acetylazulylamine, identical with the Beckmann rearrangement product of the oxime of the previously oriented mono-acetylazulene[198].

A number of disubstituted azulenes have been prepared, including the diacetyl derivative; and the second substituent is tentatively postulated as being in position 3[196]. In addition, indirect evidence has been obtained which further indicates electrophilic substitution in position 1. Thus whereas benzene diazonium chloride[199] or sulphur trioxide in dioxan[200] failed to react with 1:3-disubstituted azulenes, both reacted with mono-substituted derivatives, the sulphonic acids being characterised as their methyl esters.

The substitution reactions of azulene can be interpreted qualitatively in terms of a cyclised fulvene (276), or a cyclised heptafulvene (277), depending on which ring is involved. This notion also finds expression by considering the transition state or reacting complex in electrophilic substitution to be stabilised by the formation of the vinyl tropylium cation (279), or the corresponding cyclopentadienide anion (278) in the case of nucleophilic substitution. Attack by acylating agents activated by catalysts of the Friedel-Crafts type is common to both benzenoid aromatic systems, and as

indicated above, azulenes. Uncatalysed acylation, involving guaiazulene and acyl bromides(exceptionally oxalyl chloride) has been demonstrated, indicating a high degree of inherent polarisability in the attacked molecule in contrast to analogous reactions in the benzenoid series[194]. Guaiazulene undergoes acid catalysed condensation with aldehydes and ketones to give fulvene type salts (280), and from spectral evidence it is adduced that the 1- position is involved[195]. Though a considerable proportion of the azulene present is in the form of the azulenium cation, this reaction is better regarded as the attack of an acid activated carbonyl component on an essentially highly polarisable structure. In so far as reactions of guaiazulene are typical of the parent hydrocarbon, they are in conformity with the concept of the tropylium transition state (279).



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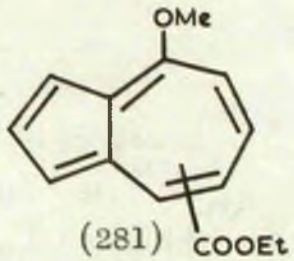

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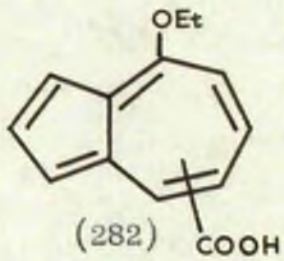

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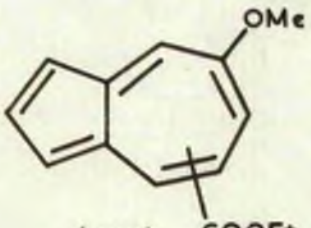

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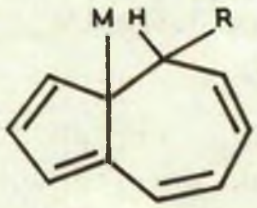
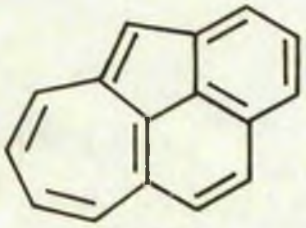


(284)

Ethoxycarbonyl - 4 - methoxyazulene (281), prepared by diazoacetic ester addition to 4 - methoxyindan followed by dehydrogenation, suffers a nucleophilic displacement in the presence of ethanolic potash, ether interchange taking place to give the ethoxy acid (282). An analogous displacement takes place in aqueous potash yielding the corresponding hydroxyazulene, but neither of the results are reproducible in the case of 4- methoxyazulene itself. More significant is the absence of ether interchange in the case of the

5-methoxy analogue (283), prepared in a parallel synthesis from 5-methoxyindan; presumably the 5 position is more resistant to nucleophilic attack.[201]. Addition of organo-metallic compounds to azulenes takes place yielding products of the type (284), and successive hydrolysis(in the absence of acid) and dehydrogenation with chloranil gives a 4-substituted derivative, repetition of the process yielding the 4:8-disubstituted derivative[202]. Both the above reactions can be interpreted quite reasonably by regarding azulene as a cyclised fulvene.



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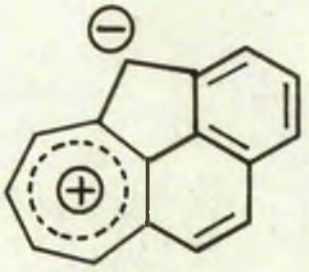

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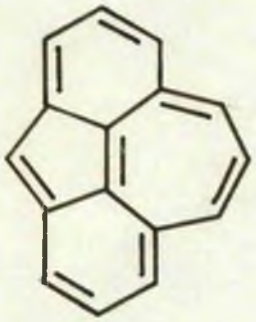

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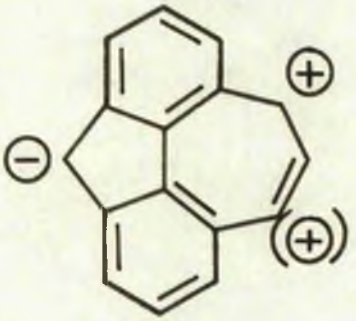


(288)

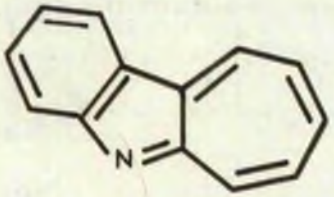
An interesting line of enquiry into the importance of potential polarisability in the fine structure of azulene entails the synthesis of cyclohepta[bc]acenaphthylene (285) and cyclohepta[def]fluorene (287). In the former numerous canonical forms are possible permitting charge separation in the azulene moiety (i.e.286), whereas in the latter only two forms involving a negative charge at carbon 2 can be depicted (288). The first compound should have well developed azulene properties which conversely should be considerably attenuated in the case of the second compound. Compound

(285) was successfully synthesised and shown to have a basicity of a very high order for azulenes, whereas compound (287) is represented only by the corresponding dihydro ester, which did not submit to dehydrogenation[203].

One of the most interesting properties of azulenes is their basicity, and the structure of the azulenium ion has already been discussed. One intuitively associates this phenomenon, in analogy with the ease of electrophilic substitution, with the inherent facile polarisability of the molecule or alternatively with the resonance energy of the resultant cation. The quantitative determination of basicity, related to the strength of acid required for complete solution, will be dealt with in (.B,III,1) but certain trends are observable. Thus with respect to azulene itself alkylation, particularly polyalkylation, results in an increase in basicity, though the effect is less pronounced with larger alkyl groups[204]. Phenylation[207], or fusion of benzene nuclei[208] produces an inverse effect. Basicity must be related to the stability of the corresponding azulenium cation, and doubtless on account of this cyclohepta[bc]-acenaphthylene(285)(see above) is unusually basic for an azulene[201]. The property has been used as a method of characterising azulenes possessing different alkyl groups substituted in the same position, as differentiation by spectral methods is impossible in these cases. In addition it has led to the development of a separation procedure, utilising the differential solubility of azulenes in acid, involving partition between acids of different strength and organic solvents[205]. In strong acid azulenes have a yellow, orange or reddish colour, and spectral measurements of the corresponding azulenium ions have been made[206].

The visible absorption spectra of azulenes are somewhat unusual. Whereas alkylation in any position in naphthalene produces a bathochromic shift of the longest wavelength absorption bands, this effect is only observed with azulene in the 1 and 5(and equivalent 3 and 7) positions, an hypsochromic shift being observed with the alter-

nate substitution products(i. e.,2, 4, 6 and 8)[209]. The data has been rationalised by Plattner and Heilbronner[210],who have shown that for di-and polysubstitution the effects are approximately additive, and the orientation of alkyl substituents on azulene has been made on the basis of spectral evidence. In addition, there are indications that groups of the electron attracting type, i.e. carboxyl[193]and[212][213][214]aldehydic[215][216]have an inverse effect on the long wave absorption bands to that described above. The data is too scattered, however, to permit of any generalisation. In contrast, the ultra-violet absorption spectra of the alkylazulenes all show a bathochromic shift with respect to azulene, but the magnitude of the shift varies with the position[217]. The two sets of spectrally distinguishable positions in the visible region have



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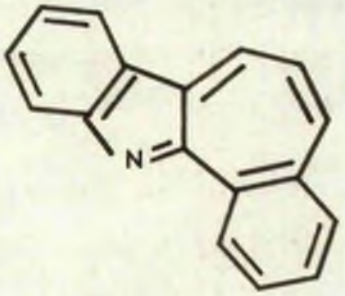

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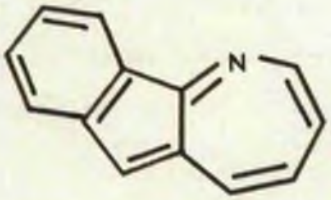

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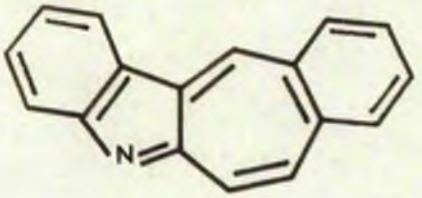

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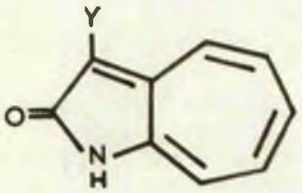

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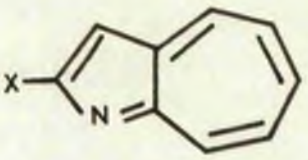

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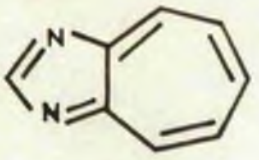
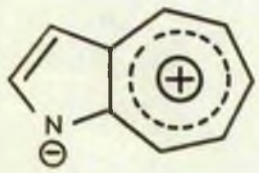


(295)

been related to the molecular orbital concept of sites of alternating high and low electron density, a feature of non-alternant aromatic hydrocarbons (molecular orbital classification of those possessing odd-membered rings), as opposed to the alternant series such as the benzenoid hydrocarbons[218][219].

A number of aza-azulenes have been synthesised. Thus 1-azabenz[b]azulene (289)[220][221] 1-azadibenz[b,h]azulene (290)[221], 4-azabenz[b]azulene (291)[222] and 1-azadibenz[b,f]azulene (292)[223] are all known. Of more interest is the preparation of the parent 1-aza-azulene by application of the malonic ester synthesis to 2-aminotropones, or of cyanacetamide to the methyl ethers of tropolones, both in the presence of sodium alkoxide, to yield (293; Y = COOEt or CN respectively), and on decarboxylation (294; Y = H). Treatment of the latter with phosphoryl chloride gives 2-chloro-1-aza-azulene (294; X = Cl) from which the parent (294; X = H) is obtained from its hydrazino derivative[224]. In addition 1:3-diaza-azulene (295) can be isolated from the base-catalysed condensation of tropolone methyl ether with thiourea followed by treatment with dilute nitric acid[225].



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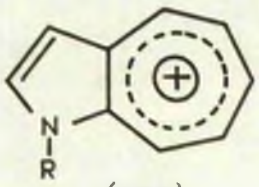

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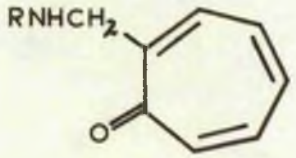
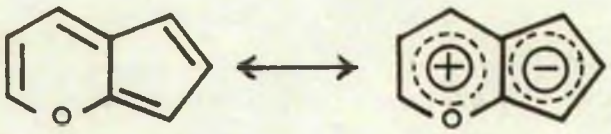


(298)

The physical and chemical properties of these aza-analogues do not seem to have been extensively investigated. The presence of a nitrogen atom in position 1 should lead to the development of considerably more polar character, through the form (296), with corresponding modifications in properties, than is the case with azulene. The nitrogen atom should be basic in nature, as in the idolenines, and not acidic, as in pyrrole. The spare '2p' electrons of the hetero atom are not required to participate in the mobile electron system, and are there-

fore available for quaternisation. Basification of the quaternary salts(297) derived from 1-oxa-azulene(294; X=H) could lead to a variety of products, but it is suggested that, in view of the resonance energy invested in the tropone structure, accession of an hydroxyl anion to the ring junction followed by ring opening to a compound of the type (298), is a possibility.

The identification of two novel heterocyclic systems in which the cycloheptatriene moiety in azulene is replaced by a six-membered heterocycle merits consideration. Thus 2-phenylbenzo[b] cyclopenta[e]pyran (300) and benzo[b]indeno [1:2-e]pyran (301) derivatives of the unknown cyclopenta[b]pyran (299) have been prepared[226].



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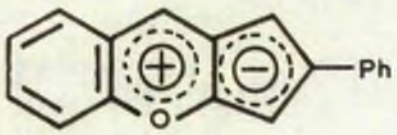

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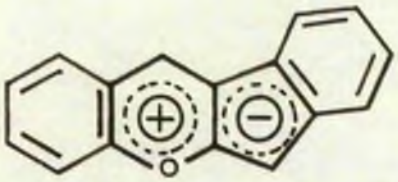

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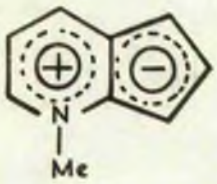

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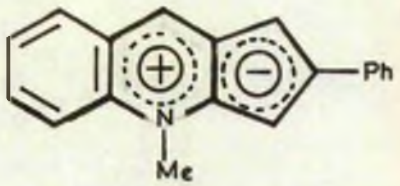


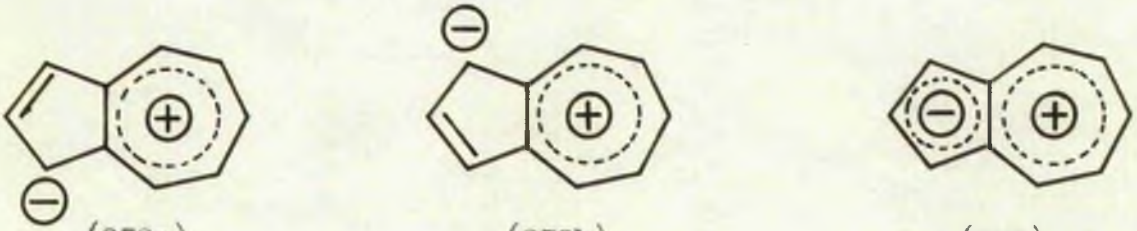
(303)

Also a number of derivatives of (302), a benzologue of the unknown (302) have been obtained[227]. The compounds (299) and (302) are isoelectronic with azulene, and consequently certain similarities in properties are to be expected. Thus far, both series of compounds seem to possess an azulene-like thermodynamic stability, and a certain amount of agreement in the ultra-violet and visible absorption spectra have been observed. The analogy with azulene is only in respect of the proposed reacting state of the latter, whose thermodynamic sta-

bility is associated principally with a mobile electron system based on the cyclodecapentaene framework (252). Accordingly the development of aromatic character displayed by this hydrocarbon is not to be expected of such hetero compounds as (299) and (302).

Approximate quantum mechanical calculations, based on the azulene molecule, of polarisation energies and π-electron densities both indicate that electrophilic and nucleophilic substitution should take place preferentially at positions 1 and 4 respectively. Furthermore, polarisation energy calculations show the radical substitution should also take place at position 4. Bond orders and bond lengths have also been calculated, the longest bond being between atoms 9 and 10[228]. The predicted positions of electrophilic and nucleophilic substitution have been confirmed experimentally, but in so far as it has been shown that the action of N-nitrosoacetanilide on azulene produces 1-phenylazulene, this does not hold true for radical substitution[229].

(252a) (252b)



(272a) (272b) (273)

On the basis of all the evidence cited above azulene emerges as a molecule possessing considerable aromatic character. It seems reasonable, at the present state of knowledge, to explain what might be designated the thermodynamic stability of azulene in terms of a mobile π-electron system disposed essentially round the periphery of

the molecule. This is identified with the 'ground' or normal state, and finds graphical representation as a hybrid of the Kekulé forms (252a) and (252b). On the other hand, the unusually facile polarisability of azulene, as evidenced by the case of electrophilic substitution in contrast to the isomeric naphthalene, can find a satisfactory theoretical explanation in the 'segmenting' of six π-electrons in each moiety to give an overall dipolar structure (273). And this, more precisely portrayed as a hybrid between the forms (272a) and (272b), is identified with the reacting state of the molecule. The possession of a finite dipole moment would seem to indicate a small contribution of the dipolar form to the normal state of azulene, but the significance of this feature taken alone in determining the properties of the molecule cannot be great. If the proposed 'ground' state electronic formulation is accepted, then this represents a unique example of the manifestation of aromatic character as a result of the delocalisation of ten π-electrons over a carbocyclic structure, formally dicyclic, though essentially monocyclic as regards the mobile electron system.

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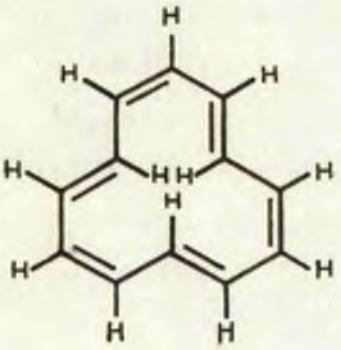
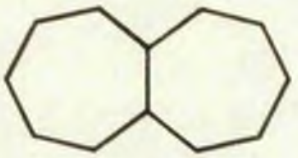
A.III.8. Twelve and Larger -Electron Systems.



(304)



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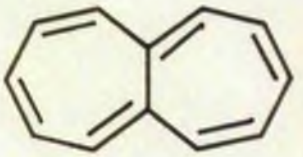
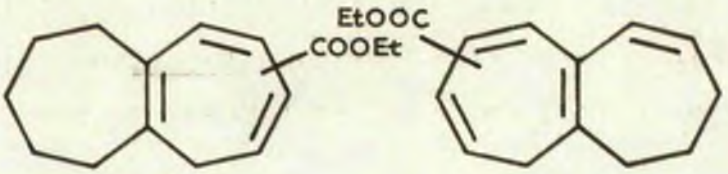


(306)

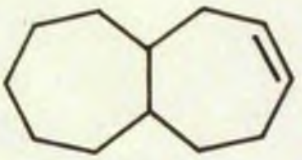
The simplest cyclic polyolefine possessing twelve π-electrons is cyclododecahexaene (304). Though neither this compound nor a simple derivative thereof has been prepared, there is good reason to suppose that it would not possess any aromatic character. Inspection of this molecule immediately indicates that those arguments which were proposed to account for the non-planarity of cyclo-octatetraene (144), and the hypothetical cyclo-decapentaene (250) have even more cogency here, and accordingly (304) is an unsuitable vehicle for the investigation of the potentialities of the twelve π-electron system. By token of the same reasoning it has been calculated that the smallest cyclopolyolefine capable of a stable existence is cyclotriacontapentadecaene, $C_{30}H_{30}$ (230).

In analogy with azulene, a bridged molecule of the bicyclo(5:5:0)dodecane type (305) may be constructed, and this hypothetical compound has been termed heptalene (306). Though such a molecule could in all probability adopt a planar configuration, there are a number of reasons why it is unappealing from the standpoint of the development of aromatic character. Each ring, being formally associated with seven, and by a process of sharing along the common bond eight π-electrons, does not correspond to any system known to possess delocalisation energy. In addition, the two moieties do not have electronically complementary tendencies, with which a considerable degree of the aromatic character of azulene in the reacting state is associated. Valence bond and molecular orbital calculations have been made for heptalene, and the most relevant conclusion is that, in conformity with pentalene, any notion of aromatic properties being conferred on this structure by virtue of resonance between two Kekulé forms, by analogy with benzene, is of dubious energetic significance (99).

A number of experiments directed towards the synthesis of heptalene have all proved unsuccessful. Catalytic dehydrogenation in the liquid phase of (307) and in the vapour phase of both (307) and (308) yielded dimethylnaphthalenes, in the latter



(307) (308)



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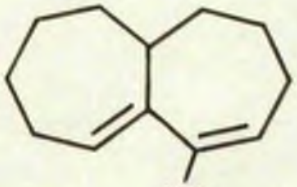

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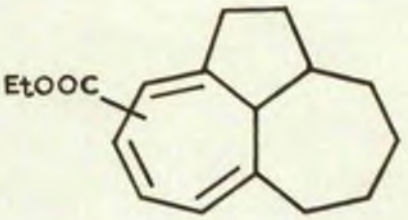
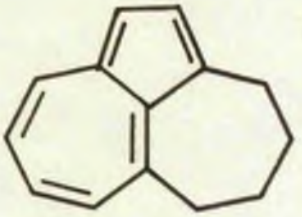


(311)



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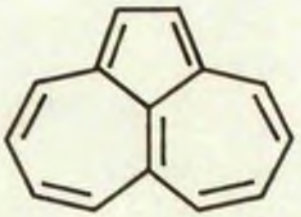
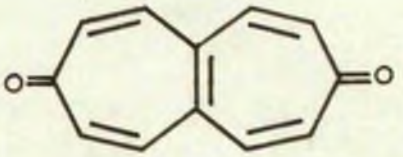


(313)

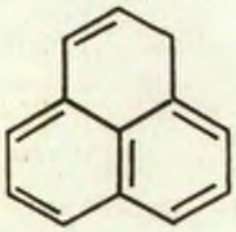


(314)

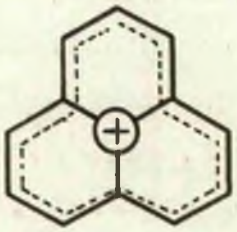
case accompanied by products tentatively identified as azulenes[231]. Catalytic dehydrogenation of decahydroheptalene (309) gave only olefinic material[232]. The synthesis of 2-methylbicyclo(5:5:0)dodecadiene, probably (310), was reported, but no attempt at dehydrogenation has been described[233]. Attempted dehydrogenation of (311) gave, not surprising, the azulene (312), which failed to eliminate any further hydrogen to give the potentially aromatic 1:10-cyclopentadienoheptalene (313)[234][235]. In spite of the lack of success evidenced above, there seems to be no reason why heptalene should not be at least as stable as pentalene, and consequently isolable. Such a compound would scarcely be expected to survive the somewhat vigorous conditions employed in catalytic dehydrogenative procedures, and more refined techniques may yet prove fruitful. A suggestion has been made that the ditropone (314) may be the only heptalene derivative to display satisfactory properties, but whereas the tropone moiety does show considerable development of aromatic character, whether this would

be retained in (314) is a matter of conjecture[236].

Inspection of formula (304) reveals that, in the adoption of a planar configuration, three 'σ' bonds are disposed centrally in such a fashion that they intersect at a unique point, subtending angles of 120° to each other. The possibility of these bonds being united through a common atom arises. Ideally, such an atom would be able to satisfy the valency requirements with a minimum of strain; and should not interact with the peripheral π-electron system. Carbon with its valency electrons in a trigonal state of hybridisation conforms in all respects save the latter, and the resultant molecule is a tricyclic carbocyclic system identifiable with perinaphthene (315). Aromatic systems, therefore, involving the perinaphthene nucleus represent the most reasonable approach to the study of the properties conferred by a mobile electron system of the type assumed to exist in the unknown cyclododecahexaene (304).



(315)



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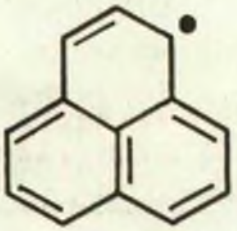
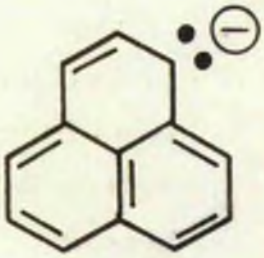


(317)



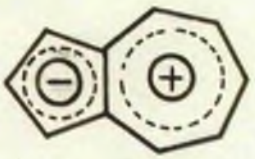
(318)

Three possibilities arise which satisfy the condition of complete peripheral conjugation i.e., the perinaphthenylium cation (316), the perinaphthenyl radical (317), and the perinaphthenide anion (318), possessing respectively systems of twelve, thirteen and fourteen π-electrons. There is abundant evidence, detailed in the next Section, that these entities do exist under suitable circumstances. In addition it has been shown that perinaphthene derivatives show properties which can only be attributed to the presence of a highly mobile electron frame-

work, as opposed to the properties expected of a cyclised allyl-naphthalene portrayed in the normal Kekul form (315). It is possibly relevant to note that the carbon skeleton in perinaphthene, composed of three fused hexagons, suggests a symmetry which is reminiscent of that obtaining in benzene itself, and with which is intuitively associated a measure of stability.

(49)

(50)



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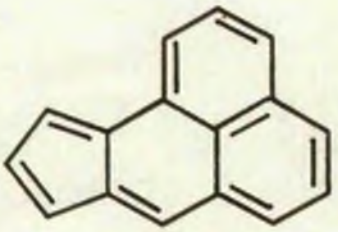

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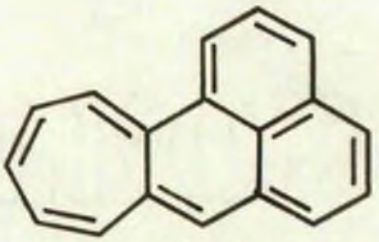
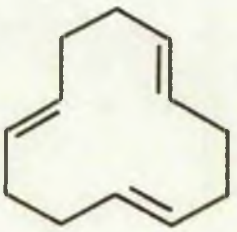


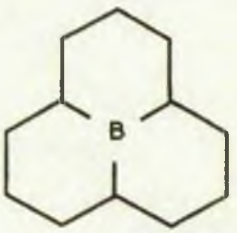
(320)

From the inference that considerable delocalisation energy obtains in the cyclopentadienide anion (49) and the cyclo-heptatrienylium cation (50), fusion of these two entities has been shown to lead to a structure which can be identified with the reacting state of azulene(273), a compound of established aromatic character. Analogously fusion of (49) and (316) and (50) with (318) should lead to structures with a similar relationship to the two hypothetical hydrocarbons, cyclopenta[a]perinaphthene (319) and cycloheptа[a]-perinaphthene(320). Accordingly, the five-membered ring in compounds of the type (320) should show properties concomitant with their counterparts in the azulene molecule. The conclusions arrived at in the former case have been substantiated by the synthesis of a benzologue of (319) and by an investigation of its properties, described in detail in Part B.

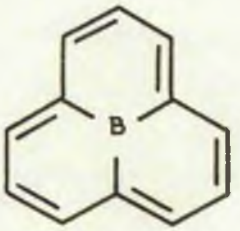
(321)



(322)



(323)



(324)

Results obtained by a study of the perinaphthene system, however, can only be applied with considerable reservation in predicting the properties of the unknown cyclododecahexaene (304). No doubt a better example for investigation would consist in a molecule with a central nitrogen atom (321), and in point of fact an attempt has been made to synthesise such a compound[237]. The structure (321) has formally a fully conjugated peripheral double bond system, but in so far as the nitrogen atom possesses two spare '2p' electrons in its valency shell, interaction between these and the mobile electron system cannot be discounted. A more satisfactory structure would involve a trivalent hetero atom, which does not possess any unused electrons in its valency shell. In this light, it is of particular interest that the addition of the boron hydride, BH_3, in the presence of a suitable catalyst such as aluminium chloride, to cyclododeca-1:5:9-triene (322), obtained from the trimerisation of butadiene, yields the centroborocyclododecane (323)[238][239]. The fully dehydrogenated derivative (324) of (323) would correspond to just such a compound as is envisaged above.

.....

Perusal of the contents of this Section reveals that no distinctive set of criteria for the development of aromatic character in the carbocyclic series emerges. The prerequisite of carbon in the trigonal valency state is an indisputable requirement for the existence

of a mobile electron system. On the other hand, the notion of resonance between two Kekulé forms as conferring π-electron stability seems only to be of significance in hydrocarbons of the benzenoid type, and possibly azulene. The association of potential delocalisability with specific numbers of π-electrons, in the narrow sense as identified with the aromatic 'sextet' theory, and in the broader sense as formulated in Hückel's Rule, would appear, on the evidence cited, to be an over-simplification of the problem. The latter hypothesis derives some confirmation from a study of the lower monocycles, but examples which would unequivocally confirm or contradict this hypothesis in the case of the larger monocycles are lacking. The role of symmetry in the mobile electron framework, though rather an abstruse quality to define, may be of importance.

In conclusion it suffices to state that, concomitant with the existence of aromatic character, certain criteria, some established and some unknown, must be fulfilled. Such fulfilment is most perfect in the case of benzene, azulene is an example of partial fulfilment, and finally examples such as cyclo-octatetraene exhibit fulfilment of a minor degree.

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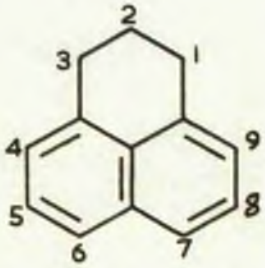
A.IV. PROPERTIES OF THE PERINAPHTHENE SYSTEM.

A.IV.1. Perinaphthene System: Nomenclature.



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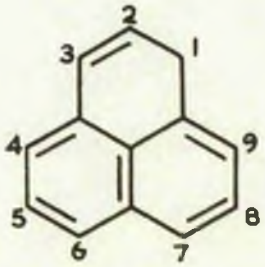

(326)

The parent aromatic system herein termed perinaphthene (326) has been designated by other systems of terminology in the literature. Thus it has been variously named the peri-naphthindene system[240], the phenalene (from phenonaphthalene) system[251], the benzonaphthene (from peri-benzonaphthalene) system[241][245] and phenalin[242][243]. Likewise the corresponding 2:3-dihydroperinaphthene (325) has been termed peri-trimethylenenaphthalene, peri-naphthindan and perinaphthane[244][248]. The use of the term perinaphthene for (326) in analogy to perinaphthane for (325) first proposed by Fieser and Hershberg[249], seems to have much to commend it, and this nomenclature has been adopted by the Chemical Society[250]. Accordingly it will be used solely throughout the thesis, in conjunction with the ring-numbering (326) also approved by the Chemical Society[250]. Nevertheless in a great deal of the literature on this topic, excepting the more recent, alternative systems of terminology and numbering have been used exclusively.

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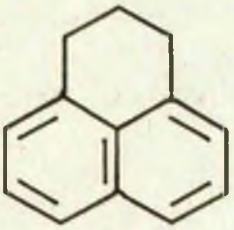
A.IV.2. Perinaphthenone Preparation.

In their classical studies of the oxidation of pyrene (327) by chromic acid, Bamberger and Philip (1887)[246] obtained in addition to a mixture of pyrene quinones, a dicarboxylic keto acid, $C_{15}H_{18}O_5$, and a

tetracarboxylic acid, $C_{14}H_8O_8$, both of which readily anhydridised, and which were subsequently decarboxylated to a ketone, $C_{13}H_8O$, and naphthalene respectively. The ketone was further oxidised to a



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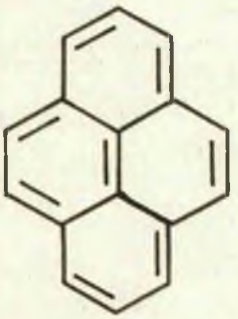

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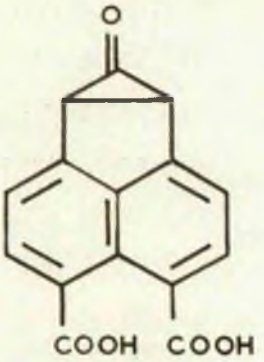

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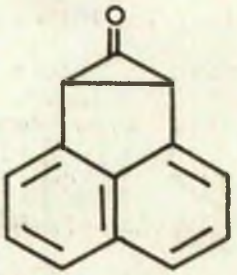

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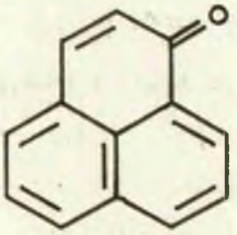
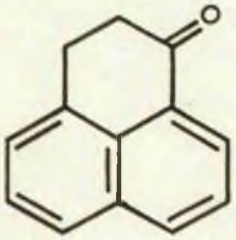


(330)

naphthalene dicarboxylic acid, also readily anhydridised, and this on decarboxylation likewise yielded naphthalene. On the basis of the above evidence these workers proposed formula (328) for the dicarboxylic keto acid, which they termed 'pyrene acid', and formula (329) for the ketone, termed 'pyrene ketone'. Goldschmiedt(1883) suggested that either formula (329) or (330) could account for the structure of the ketone[247], and this latter proposition appeared to find general acceptance, and though rigid proof was not forthcoming, was incorporated in 'Beilstein's Handbuch'[243]. Langstein(1910), on repetition of Bamberger's work obtained the 'pyrene acid' and on hydrogenation with phosphorus and hydroiodic acid followed by decarboxylation prepared peri naphthalene (325)[248].



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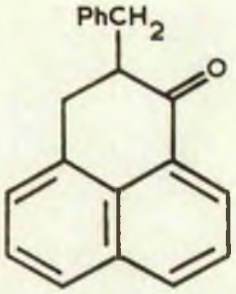

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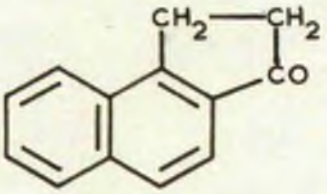
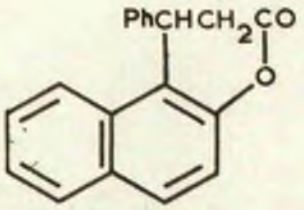


(333)

On treatment of β-(1-naphthyl)-propionyl chloride (obtained from 1-bromomethylnaphthalene by the malonic ester synthesis) with aluminium chloride in ligroin, Meyer and Sieglitz (1922) obtained a small quantity of yellow ketonic material which they believed to be 2:3-dihydroperinaphthen-1-one (331)[251]. By an analogous cyclisation procedure involving α-benzyl-β-(1-naphthyl)propionyl chloride, von Braun, Mans and Reinsch(1929) were able to isolate from the resulting mixtures of ketones 2-benzylperinaphthan-1-one(332), subsequently synthesised by the condensation of benzaldehyde with (331) (prepared according to the method of the previous authors) followed by catalytic hydrogenation of the exocyclic double bond of the product[252]. On attempted repetition of the work of Meyer and Sieglitz, Cook and Hewett(1934) observed that though the crude cyclisation product bore a resemblance to that described in the original work, only the yellow perinaphthenone (330), presumed identical with Bamberger's 'pyrene ketone', could be isolated. The same ketone was prepared in moderately good yield by treatment of β-(1-naphthyl)-propionic acid with stannic chloride, though in this case it was accompanied by a small amount of colourless ketone, either the authentic 2:3-dihydroperinaphthenone (331) or the isomeric 4:5-benz-1-hydrindone (333)[253].

Notwithstanding the observations of Cook and Hewett, Darzens and Levy(1935) obtained from the cyclodehydration of β-(1-naphthyl)-propionic acid with aluminium chloride in nitrobenzene a product which corresponded to 2:3-dihydroperinaphthen-1-one (331)[254]. β-Naphthol

and cinnamic acid were condensed in the presence of sulphuric acid to give 3:4-dihydro-4-phenyl-coumarin (334), hydrolysed and methylated to β-phenyl-β-(2-methoxynaphthyl-1)-propionic acid (335). The acid chloride from (335), when treated with aluminium chloride, gave what



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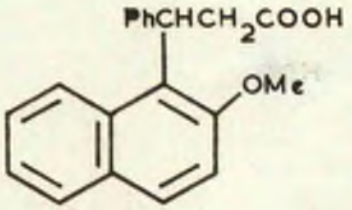

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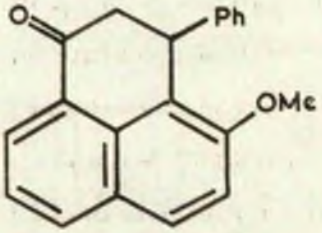

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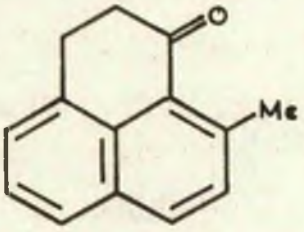
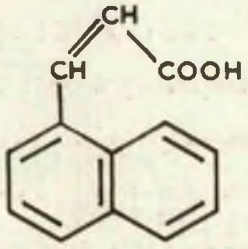


(337)

Koelsch(1936) considered to be 4-methoxy-3-phenyl-2:3-dihydro-perinaphthen-1-one (336)[255]. On cyclisation of β-(2-methylnaphthyl-1)-propionyl chloride by a method similar to that of Meyer and Sieglitz, Klyne and Robinson isolated a faintly yellow product which analysed correctly for 9-methyl-2:3-dihydroperinaphthen-1-one (337)[256].

The somewhat anomalous results obtained by various workers in this field was clarified by the preparation, due to Fieser and Gates(1941), of the authentic 2:3-dihydroperinaphthen-1-one in high yield by the cyclodehydration of β-(1-naphthyl)-propionic acid by the action of anhydrous hydrogen fluoride. The compound, which was colourless, was identified by Clemmensen reduction to the known perinaphthane[257]. Perusal of the data which these workers obtained form a study of the pure product revealed that previous cyclisation procedures had in fact

resulted in the formation of the dihydro-ketone (331), contaminated to a greater or lesser extent with a significant amount of yellow dehydrogenation product. A by-product of this reaction appeared to be identical with the colourless dihydro-ketone of Cook and Hewett, and was assigned the structure of 4:5-benz-1-hydrindone (333). The ring closure of β-(1-naphthyl)-propionic acids using β-alkylated propionic acids on the one hand, methoxynaphthalenes on the other, and polyphosphoric acid in addition to hydrogen fluoride as cyclising agent has been exhaustively investigated. Invariably the resultant perinaphthanone, though the major product, is accompanied by the corresponding indanone[258][259][260].



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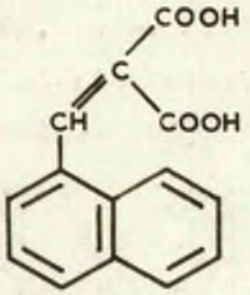

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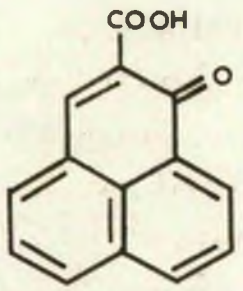


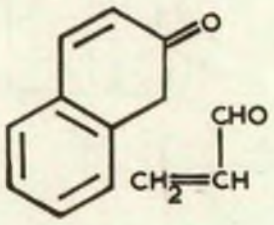
(400)

The analogous cyclodehydration of β-(1-naphthyl)-acrylic acids directly has been studied by Lock and Gergely. The acrylic acid (338), prepared from 1-methylnaphthylketone failed to cyclise on treatment with anhydrous hydrogen fluoride, though the closely related malonic acid (339) behaved normally towards this reagent to yield perinaphthene-2-carboxylic acid (400). The existence of (338) in the trans configuration was proposed to account for its failure to cyclise, since after successful racemisation by ultra-violet radiation the resulting cis-naphthylacrylic acid underwent ring closure[261].

A process has been developed for the preparation of perinaphthenenes on an industrial scale. Thus on heating together α-or β-naphthol and glycerol in sulphuric acid in the presence of an oxidising agent such as sodium nitrobenzenesulphonate followed by dilution in an excess

of water, perinaphthenone is precipitated. It has been suggested that the reacting entities are the keto forms of α- or β-naphthol and acrolein as shown in (401) and (402). Ferric chloride or arsenic acid may replace sodium nitrobenzenesulphonate, and dihydroxynaphthalenes, aminonaphthols, halonaphthols, naphtholcarboxylic acids and naphtholsulphonic acids have been used as starting materials[262]. The preparation has been adapted to the laboratory scale by Silbermann and Barkov[263], and Fieser and Hershberg[249], the latter authors obtaining a yield of about 26%. This process has recently been reinvestigated with a view to determining the optimal conditions[264].

Vollmann et al, in the course of their extensive studies on pyrene, have repeated the work of Bamberger, and shown 'pyrene ketone' to be identical with perinaphthenone prepared as above. This is of particular interest in so far as it represents the only direct comparison to have been made between these two compounds, whose identity has nevertheless been tacitly assumed[265].



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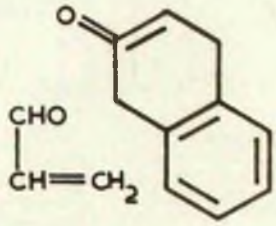

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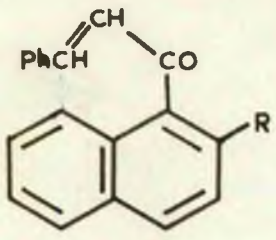

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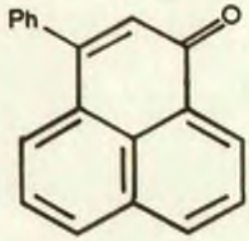

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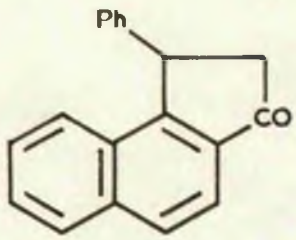

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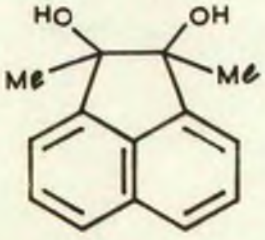

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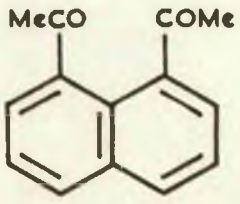

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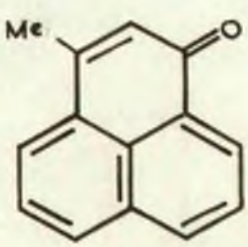
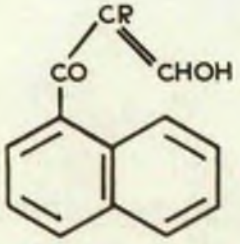


(408)

A number of perinaphthenone syntheses are of interest in a particular rather than a general sense. Originally it was considered that treatment of 1-cinnamoylnaphthalene (403; R = H) with aluminium chloride gave (404)[266], though it has been subsequently shown that dephenylation occurs simultaneously and the product is in fact perinaphthenone itself. This reaction has been applied to the preparation of 9-hydroxyperinaphthenone (430) from 1-cinnamoyl-2-methoxynaphthalene (403; R = CH_3O)[291]. Cyclodehydration of β-(1-naphthyl)-cinnamic acid by sulphuric acid yields a mixture of the appropriate perinaphthenone (404) and the 4:5-benzindan-1-one (405)[271]. 1:2-Dimethylacenaphthene-diol (406) is cleaved by lead tetra-acetate to peridiacetylnaphthalene (407). Piperidine catalysed intramolecular condensation of (407) results in the formation of 3-methylperinaphthen-1-one (408)[267].



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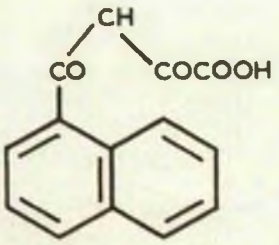

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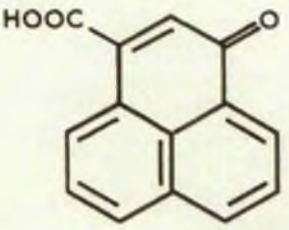

(411)

The most satisfactory laboratory preparation of perinaphthenone itself involves the cyclodehydration of the corresponding oxymethylene-naphthyl ketone, obtained as the sodio derivative from the base-catalysed condensation of ethyl formate and 1-methylnaphthylketone. This reaction was originally developed with a view to industrial application, and in this connection the suitability of hydroxymethylene ketones of the general formula (409; R = aryl, alkyl or H) with a free position peri to the keto group, and condensing agents such as concentrated sulphuric or phosphoric acids are indicated[268]. Lock and Gergely obtained yields of perinaphthenone of the order of 80% in an analogous laboratory preparation utilising 87% sulphuric acid[269]. The cyclo-

dehydration of the acid (410) in 88-90% sulphuric acid has been achieved to give the resultant 3-carboxy-perinaphthen-1-one (411), presumably by similar mode of reaction to the above cyclisations. The acid (411) undergoes a modified Curtius rearrangement to the 3-amino derivative[270].

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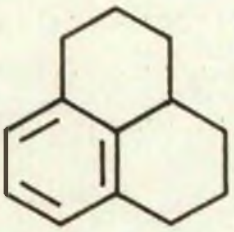
A.IV.3. Perinaphthene: Preparation.



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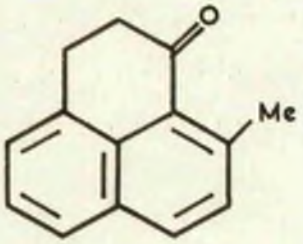

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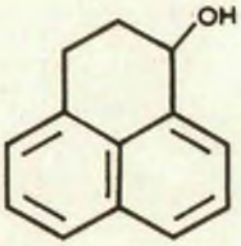

(413)

The parent hydrocarbon, perinaphthene, has not proved to be capable of such ready isolation as did the corresponding ketone, perinaphthenone. von Braun and Reutter(1926), in a somewhat lengthy synthesis, prepared the hexahydroperinaphthane (412), and observed that no useful material could be obtained from it by simple dehydrogenation[272]. Perinaphthenone suffered catalytic hydrogenation using a two year old batch of Raney nickel giving perinaphthan-1-ol (413) (freshly prepared catalyst gave a considerable amount of phenolic material)[249]. Attempted dehydration of the latter by Fieser and his co-workers by means of sodium bisulphate, the Tschugaeff reaction or by way of the chloride respectively was without positive outcome[273]. In the structural investigation of the veratrine alkaloid cevine, five hydrocarbons were obtained as a result of a selenium dehydrogenation reaction, four of which proved to be fluorene derivatives, the fifth being suspected identical with the unknown perinaphthene. The treatment of perinaphthenone with selenium at elevated temperatures, undertaken by Craig, Jacobs and Levin in an attempt to confirm this, yielded, after rigorous purification, a small quantity of perinaphthane only[274].

The first successful synthesis of perinaphthene was accomplished

by Lock and Gergely(1944). These workers obtained a very small yield of this hydrocarbon by the Wolff-Kishner procedure involving the hydrazone of perinaphthenone[269]. Perinaphthene has been more recently isolated(Hochstein,1949) as a result of the reduction of perinaphthenone by means of lithium aluminium hydride[275]. On repetition of the work by Boekelheide(1950) it was found that perinaphthene accounted for only 14% of the reduction product, the remainder being comprised of perinaphthanone(65%) and phenolic material(12%). The atypical hydride reduction is reproducible for all perinaphthenones to a variable extent, and its significance will be commented upon later. Currently the most satisfactory synthesis of perinaphthene is an adaptation of that applied to the preparation of a methylperinaphthene(see below). Thus the readily available perinaphthan-1-one is reducible to perinaphthan-1-ol by action of lithium aluminium hydride, and this can be subsequently dehydrated by ethanolic hydrogen chloride to give yields of perinaphthene ranging from 65 to 85%[276].

It is pertinent in this context to detail attempts to obtain a methylperinaphthene. Klyne and Robinson(1937) who considered that in view of the great symmetry of the system, methylperinaphthene should exist in six readily interconvertible tautomers, attempted to synthesise such a compound by the intramolecular acylation of β-(2-methylnaphthyl-1)-propionyl chloride to the expected ketone (337). Reduction of the latter by the method of Meerwein-Ponndorf gave the corresponding 9-methyl-perinaphthan-1-ol which failed to succumb to dehydration by the Tschugaeff reaction. The amine obtained from the oxime of (337) gave no satisfactory results on application of Hofmann's procedure[256].

Craig, Jacobs and Levin(1941) were successful in isolating a small quantity of a methylperinaphthene from the interaction of perinaphthenone and methyl magnesium iodide, and in addition obtained an oxygenated compound, possibly a methylperinaphthenone in an analogous fashion to the production of perinaphthanone in the lithium aluminium hydride reduction of perinaphthenone[274]. Methylperinaphthene was subsequently obtained by Fieser(1942) by the dehydration of 9-methyl-

perinaphthan-1-ol using ethanolic hydrogen chloride, a process which later proved successful in the preparation of perinaphthene itself[273]. The structure of the resulting product from the above synthesis has been studied and will be dealt with in (A,IV,7).

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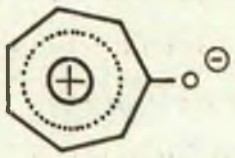
A,IV,4. Perinaphthenone: Chemical Properties.



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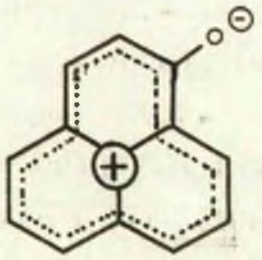


(414)

As a consequence of the hypothesis regarding the perinaphthenylium cation outlined in (A,III,8), it follows as a logical development that perinaphthenone bears a formal resemblance to tropone. Properties which were associated with the dipolar form of tropone (96) should have their counterpart in perinaphthenone as a result of the dipolar form (414). Once again no attempt will be made to justify the concept of perinaphthenone existing wholly or even to a great extent in the form (414), and like so many of the systems discussed, a highly polarisable molecule is visualised which is prone to revert to form (414) in the reacting state. It is possibly more accurate to state that an electron migratory tendency from the carbocyclic π-electron system to the extracyclic oxygen atom is to be inferred from the portrayal of perinaphthenone as (414).

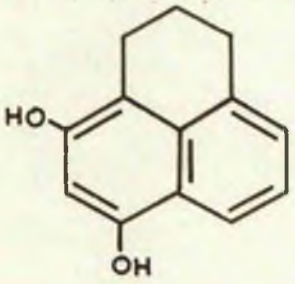
Perinaphthenone crystallises in yellow needles, m.p. 156°[277]. It dissolves in concentrated hydrochloric acid to give a gold to orange coloured solution with an intense green fluorescence from which it is recoverable on dilution[253]. An oxime, m.p. 166-167°, a hydrazone m.p. 125-130° and a semicarbazone which sinters about 210° have been prepared[269]. Perinaphthenone is soluble in the majority of organic

solvents, this being more true of the polar variety.

The first recorded attempt to reduce perinaphthenone involved the treatment of 'pyrene acid'(perinaphthenone-6:7-dicarboxylic acid)(328) with red phosphorus and hydrogen iodide to yield after decarboxylation, perinaphthane (325)[248]. Reduction with zinc and hydrochloric acid has also been observed to give a very low yield of perinaphthane[263]. Perinaphthenone suffers catalytic hydrogenation at atmospheric pressure in the presence of Raney nickel to give perinapthan-1-ol accompanied by a variable amount of phenolic material, though the former is considerably increased and the latter diminished utilising old and presumably less reactive catalyst. Perinaphthanol and perinaphthane result from pressure hydrogenation in the presence of copper chromite catalyst and even the naphthalene nucleus succumbs to reduction under forcing conditions[249][273]. The catalytic reduction of 1:3-diketoperinaphthane (3-hydroxyperinaphthenone) (421) in ethanolic solution using Adam's platinum oxide catalyst has been shown to give 4:6-dihydroxyperinaphthane (415)[289]. The production of a phenolic compound here and also in the case of the lithium aluminium hydride reduction of perinaphthenone has resulted in the suggestion of an analogous reaction mechanism pertaining in both. The essentially different nature of the two reactions renders this doubtful.

The lithium aluminium hydride reduction of perinaphthenone takes an abnormal course, the products being perinaphthene (14%), perinaphthanone (65%) and unidentified phenolic material (12%)[275][276]. The first step in this reduction is presumed to be the normal reduction of the keto-group to a secondary alcohol followed by isomerisation to the enol (416), from which may be derived very simply perinaphthanone and the phenolic material. However this mechanism does not account for the formation of perinaphthene, which must involve rupture of a carbon-oxygen bond, and in view of the fact that yields of a perinaphthene homologue of the order of 70% have been obtained in an identical reaction cannot be the principal mode of reaction. This phenomenon is reproducible to a greater or lesser extent in the case of all perinaphthenones investigated.

Peropyrene (418) together with perinaphthane, are the products when perinaphthenone is heated with zinc dust in a sodium chloride/zinc



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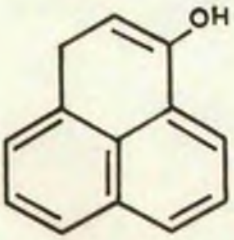

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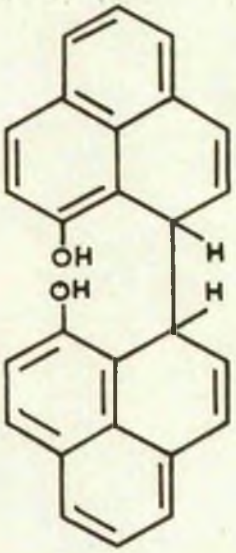

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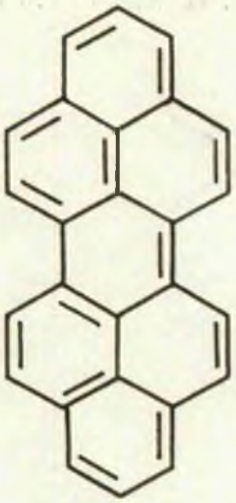
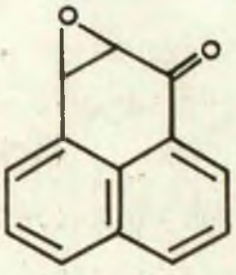


(418)

chloride melt. It is suggested that a bimolecular reduction product (417) is first produced which undergoes spontaneous intramolecular dehydration[278].

The action of selenium on perinaphthenone at elevated temperatures gives perinaphthane in a very low yield[274]. Doubtless perinaphthene, if formed at all, is insufficiently stable to withstand such vigorous reaction conditions, and though suffering some reduction, is mainly destroyed. Perinaphthenone is attacked slowly by hydrogen peroxide in the presence of sodium carbonate to yield an epoxide, probably with structure (419). The epoxide was cleaved by pouring its solution in concentrated sulphuric acid on to ice and the product was presumed to be the 1:2-diketone (420) as it displayed different properties from the 1:3-isomer (421)[273]. Vigorous oxidation with chromic acid degrades perinaphthenone to naphthalic acid[246].

As a consequence of the hypothesis that delocalisation energy is invested in the perinaphthenylium cation, a similar property should obtain in the conjugate acid, the hydroxyperinaphthenylium cation (422) resulting from accession of a proton to the oxygen atom in form (414). In conformity with this hypothesis, and in analogy to tropone, perinaphthenone is unusually basic for a ketone, dissolving reversibly in concentrated hydrochloric acid to give a bright orange solution. This property is of considerable value in the separation of perinaphthenones from other ketones and non-basic material. The analogy with tropone is extended further in that crystalline salts have been isolated from the interaction of perinaphthenone with strong acids. Thus a sulphate has been obtained from perinaphthenone and 68% sulphuric acid dissolved in excess acetic acid, and likewise a nitrate of variable composition by the direct treatment of the ketone with nitric acid. A hydrochloride and a hydrobromide have been prepared by passing the appropriate hydrogen halide through a benzene solution of the ketone, though the latter salt did not contain a stoichometric amount of chlorine. All the above salts



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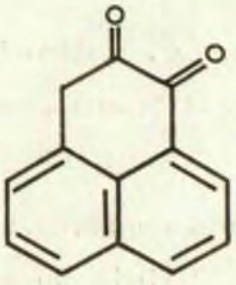

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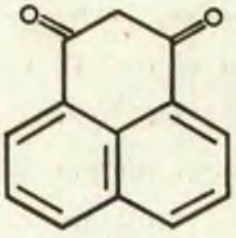

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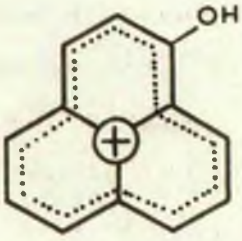
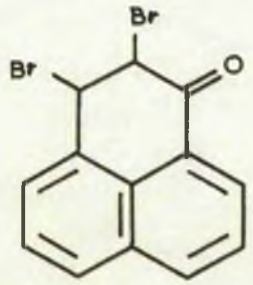


(422)

are yellow crystalline solids with characteristic melting points, but the halides appear to evolve hydrogen halide slowly on standing and are readily hydrolysed by water[279]. The dissociation constant (pK_a) for the conjugate acid (422) as well as those derived from benzanthrone and benzalacetophenone have been determined by a method involving the spectrophotometric estimation of the partition of the appropriate ketone between acid and an immiscible organic solvent. It is concluded from the results of the above that perinaphthenone is more readily protonated than the other ketones[280].



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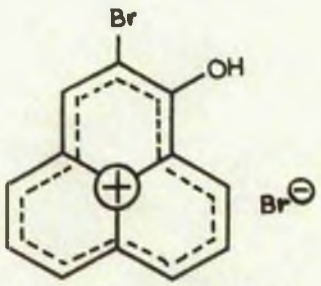
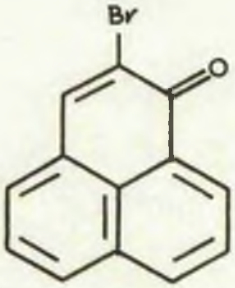


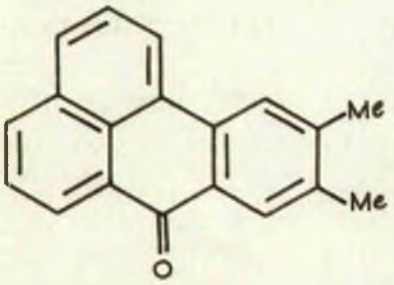
(424)



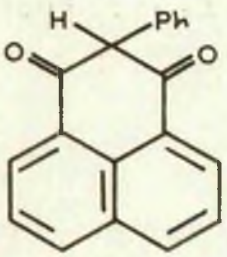
(425)

Interaction of bromine and perinaphthenone in benzene or acetic acid results in the formation of the yellow dibromide (423) which slowly evolves hydrogen bromide on standing, and rapidly loses the elements of hydrogen bromide on treatment with boiling ethanolic sodium carbonate or ammonia, to yield what is presumed to be 2-bromo-perinaphthenone (425). If the bromination is conducted in acetic acid, a colourless complex with the formula $(C_{13}H_8O)Br_2$ forms initially which slowly reverts to the yellow dibromide (423). Furthermore on heating the dibromide in a sealed tube, in addition to the starting material a bromoperinaphthenone hydrobromide (424) is formed. The latter salt is also obtained by heating a solution of bromine and perinaphthenone in acetic acid, by heating the dibromide in chloro-benzene solution, or alternatively by treatment of 2-bromoperinaph-thenone with hydrogen bromide in a suitable solvent. Prolonged heating of a solution in acetic acid of the ketone and bromine gives the ultimate product (425) in 96% yield. As a consequence of the above

series of reactions, which have also been observed in the case of chlorination, it has been reasoned that the bromination of perinaphthenone takes the course (423) to (425). The occurence of an intermediate addition compound in the substitution of perinaphthenone is reminiscent of the bromination of tropone. The ketone is readily regenerated from the complex by treatment of the latter with sodium thiosulphate[281][282][283].



(426)



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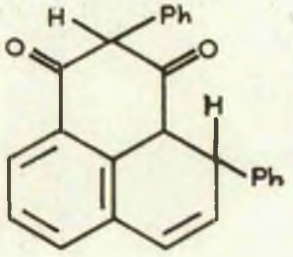
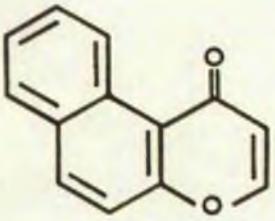


(428)

Attempts to utilise perinaphthenone in the Michael condensation, or as the dienophile component in the Diels-Alder reaction have met with no success, and it is also inert to Friedel-Crafts type condensations unless under forcing conditions. Thus such a condensation was effected with benzoyl chloride by heating the components to 140° together with a mixture of aluminium and zinc chloride to yield a product later identified as 2-benzoyl-1-perinaphthenone. Notwithstanding the resistance of the ketone itself, perinaphthenone - 2 - carboxylic acid succumbs to diene addition, and with 2:3 - dimethylbutadiene the fully aromatised adduct (426) is obtained, though using mild conditions a di - and tetrahydro - adduct are isolable[278].

Perinaphthenone reacts with Grignard reagents, and the normal mode of addition appears to be 1 : 4. Thus the product from the interaction of phenyl magnesium bromide and (427) has been shown to be (428)[290], whereas from the interaction of this Grignard reagent and perinaphthenone itself 9-phenylperinaphthenone was isolated[291]. A similar mode of addition is presumed to have occured in the case of

perinaphthenone and methyl magnesium iodide[274].



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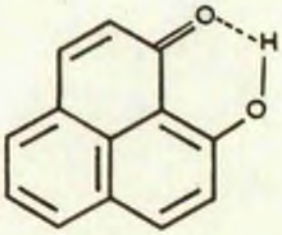

(430)

It is pertinent to note that perinaphthan -1:2 - dione (420) and perinaphthan - 1:3 - dione (421) bear a formal resemblance to the α- and β-tropolones, though no investigations have been carried out with this potential relationship in mind. However 9-hydroxyperinaphthenone (430), prepared both by the cyclisation of 1-cinnamoyl-2-methoxy-naphthalene under the action of aluminium chloride in benzene[291], and by rearrangement of 5:6-benzochroman-4-one (429) by fusion with aluminium chloride[292], has been shown to possess an unusual degree of hydrogen bonding between the hydroxyl and keto groups. This is reminiscent of a similar phenomenon which occurs in α-tropolone and doubtless the theoretical interpretation lies in the similar environment of the keto group in each case.

Nucleophilic substitution has been demonstrated for this ketone in that when the bromo-ketone (425) is reacted with an excess of morpholine or piperidine, mainly the 3-morpholino and 3-piperidino-perinaphthenones are obtained if the reaction is carried out at room temperature. At elevated temperatures the 2-isomer predominates in both cases[285].

Perusal of the above reveals that the suggested similarity between tropone and perinaphthenone finds ample justification from a

consideration of such properties as the basicity, lack of dienophile activity, electrophilic and nucleophilic substitution, displayed by the latter.

A number of oxonium salts, for example $(C_{13}H_8O_2)$ H $FeCl_4$, $(C_{13}H_8O)_2$ $SnCl_4$ and $(C_{13}H_8O_2)$ $SbCl_5$, have been prepared by the action of sodium nitrobenzene sulphonate and the appropriate component[263]. Perinaphthenone in common with certain other polycyclic ketones forms sulphoxides on interaction with sulphur trioxide in inert solvents. Stable at room temperature, these compounds decompose on heating. Likewise, nitrosoxide formation has been observed for perinaphthenone on treatment with nitrogen dioxide in a suitable medium. These latter compounds are both stable and crystallisable, but are decomposed by water.

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A.IV.5. Perinaphthenone: Physical Properties.

In an examination of the infra-red spectral data of the tropone series, the observed low carbonyl stretching frequency was associated with conjugation of the latter group with the carbocyclic mobile electron system. This phenomenon is again in evidence in the case of the perinaphthenones, and a uniform theoretical interpretation is presumed to apply in both these classes of compounds[285][286][287]. The low carbonyl stretching frequency is demonstrable for all the known perinaphthenones, as perusal of the data detailed in table II will confirm. Ultra-violet and visible absorption spectra of the perinaphthenones are not, in the light of present knowledge, of the same fundamental significance.

Polarographic investigation of the first wave of perinaphthenone and a number of simple derivatives has shown that reduction proceeds reversibly, and with remarkable ease as compared with the corresponding process in benzanthrone and benzalacetophenone. The essential process is one electron addition to the

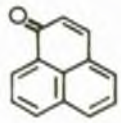
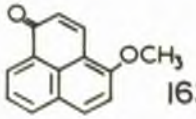
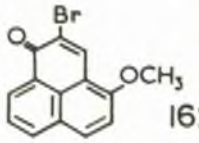
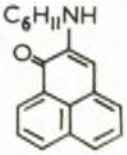
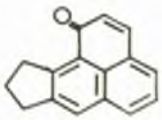
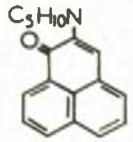
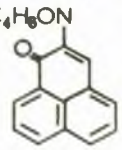
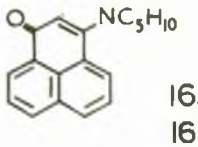
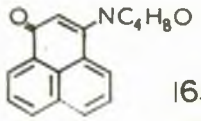
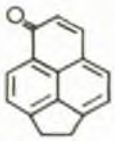
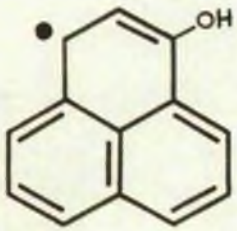
	Wave Number, cm^{-1}	Reference
	1637	(286)
	1632	(48)
	1628	(48)
	1632 1615	(286)
	1637 1621	(C,V,3)
	1630 1619	(286)
	1637 1621	(286)
	1633 1611	(286)
	1633 1611	(286)
	1634 1618	(284)

TABLE II. Carbonyl stretching frequencies in the perinaphthenone series.

molecule with concomitant formation of the 1-hydroxyperinaphthenyl radical (431). An outcome of the investigation is that 9-hydroxyperinaphthenone (430) shows considerable resistance to radical



(431)

formation as opposed to the parent compound, and it is suggested that strong hydrogen bonding as proposed in (A,IV,4) supplies additional resonance energy to the unreduced compound. Contrariwise, perinaphthenone-3-carboxylic acid (411) displays greater ease of radical formation than the parent ketone, and it is presumed that the electron-attractive effect of the carboxyl group promotes electron addition at the oxygen site, an effect which disappears when the carboxylate ion is formed. The above results are in conformity with the predicted existence of the perinaphthenyl radical[280].

The acidity constant ($p.k._a$) of the conjugate acid (422) was determined spectroscopically by partitioning between mixtures of sulphuric acid corresponding to various Hammett function values(H_o) and chloroform. The results are indicative of the ready formation of the hydroxyperinaphthenylium cation (422) as opposed to the corresponding cation derived from benzanthrone or benzalacetophenone, in accord with the proposed stability of the perinaphthenylium cation (316)[280]. The data from this and the previous investigations are tabulated in table I.

	$-E_{\frac{1}{2}}$ V(S.C.E.)	pKa (conjugate acid)	pKa (free radical enol).
perinaphthene-9-one	0·34	-3·9	9·3
perinaphthen-9-one-7-carboxylic acid	0·24	-3·4	——
perinaphthen-9-one-7-carboxylate (ion)	0·34	——	9·0
1-hydroxy-perinaphthen-9-one	0·62	-4·8	8·0
perinaphthen-9-one-1-oxide (ion)	0·49	——	13·0
benzanthrone	0·47	-5·8	10·8
benzalacetophenone	0·52	-7·6	10·4

TABLE I Half Wave Potentials and Acidity Constants of Perinaphthenone and Derivatives[280].

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A.IV.6. Perinaphthene: Properties[276].

Perinaphthene has only recently become available in quantity, and consequently it has not been the subject of such intensive investigation as the corresponding ketone. Perinaphthene crystallises in colourless plates, m.p., 85-86° which become discoloured in a matter of a few hours, and completely black in a few days. Samples stored under nitrogen appear to be stable indefinitely, though some discolouration is inevitable. Atmospheric oxidation to perinaphthenone and catalytic hydrogenolysis to perinaphthane have been demonstrated, though the former transformation can be achieved, giving an 83% yield of ketone, by the use of chromic acid.

As a result of the postulated existence of the perinaphthenide anion (318), perinaphthene would be expected to be acidic, showing similarities to cyclopentadiene, indene and fluorene, and this has been demonstrated experimentally. Thus a deep red solution is obtained,

resulting from the formation of the lithio derivative, on treatment of an ethereal solution of perinaphthene with phenyl lithium. Interaction of perinaphthene with potassium methoxide yields the potassio derivative. Alkylation of the lithio derivative with methyl iodide yields a methyl perinaphthene, identical with those previously prepared, by transposition of the methyl group from its original site through migration of the double bonds. A red, fulvene-type compound has been obtained by the base-catalysed condensation of perinaphthene with benzaldehyde.

A deep red colour was obtained in the Vanscheidt test[288], which rapidly changed to olive green. The Vanscheidt test, involving colour development on the addition of potassium hydroxide and pyridine to a solution of the appropriate hydrocarbon in acetone, is supposedly typical of cyclopentadiene and its ring homologues with an exposed methylene group. Bromination of perinaphthene in the cold readily gave a dibromide, but attempted dehydro-bromination gave only deeply coloured green blue solutions. Reaction of perinaphthene with N-bromsuccinimide likewise gave only highly coloured solutions. In another experiment the colour of a solution of triphenylmethyl was altered from yellow-orange to olive green on the addition of perinaphthene. The significance of the colour development observed in the above reactions will be invoked in connection with the transformation of the perinaphthenide anion to the perinaphthenyl radical which is dealt with in (A,IV,8).

As regards the stability of the perinaphthenide anion it has been established that perinaphthene has an acidity intermediate between triphenylmethane and cyclopentadiene. The possibility of perinaphthene forming compounds of the 'ylide' type similar to those described for cyclopentadiene (A,II, 2), or forming 'sandwich' molecules with a transition metal (A,II,4) cannot be discounted, though thus far has not been demonstrated.

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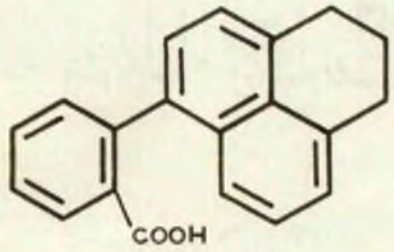
A,IV,7. Isomerisation in the Perinaphthene Series.

In addition to the properties of perinaphthene derivatives in which the formation of a cation, radical or anion is implicit, there

are a number of reactions which are not satisfactorily accounted for in terms of these entities alone, but rather on the basis of the existence of a highly mobile peripheral electron system. It was suggested by Klyne and Robinson(1938)[256] that the unusually high symmetry of the perinaphthene nucleus should result in a mono-substituted derivative existing in six readily interconvertible tautomeric forms corresponding to the equivalent 1,3,4,6,7 and 9 positions. In pursuance of this goal, these authors were unsuccessful in synthesising a methylperinaphthene by the method outlined in (A,IV,2.). This concept has not been realised in practice, but there is considerable evidence that ready isomerisation does take place. As an outcome of this attempts to prepare derivatives substituted in certain positions have been persistently frustrated by migration of the double bonds.



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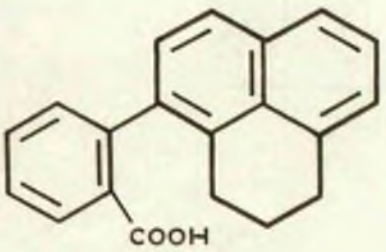
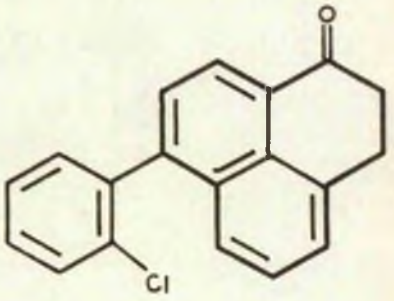


(433)

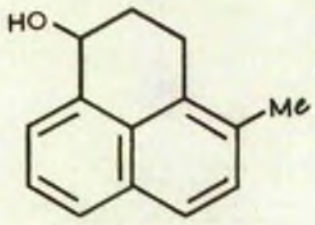


(434)

Fieser and Gates(1940)[257], in an attempt to prepare 1-(-o-chlorophenyl)-perinaphthene, reacted perinaphthanone with the appropriate Grignard reagent. On catalytic hydrogenation, followed by replacement of halogen with the cyano group, two isomeric nitriles were obtained. That neither contained the substituent in the desired position was shown by hydrolysis of the nitriles to two acids, formulated as (432) and (433) on the basis of cyclisation to known compounds. In addition, Fieser and Newton(1942)[273] prepared a methylperinaphthene by the action of methyl magnesium iodide on perinaphthanone followed by dehydration, which was believed identical with that isolated in

low yield by Craig, Jacobs and Levin(1941)[274] by direct interaction of perinaphthenone with methyl magnesium iodide. Likewise Badger, Carruthers and Cook, in an attempt to prepare a 4-methoxyperinaphthene, observed that condensation of 4-methoxyperinaphthanone with o-chlorophenyl magnesium bromide followed by dehydration, gave through rearrangement and demethylation the ketone (434) as the sole product[293].

The isomerisation of the methylperinaphthenes was thoroughly studied by Boekelheide and Larrabee(1950)[294]. These authors subjected the three carbinols (435), (436) and (437), to dehydration using ethanolic hydrogen chloride, and on repetition of the work of Fieser and Newton, and of Craig, Jacobs and Levin observed that the product in all cases was identical and suffered catalytic hydrogenation to the identifiable 4-methylperinaphthane. On the basis of the above, the product was formulated as (438). It was not possible to assign a position to the double bond in the peri ring, although oxidative cleavage using ozone and per-acids was attempted. In this connection, it is suggested that osmium tetroxide might be a more satisfactory reagent. A plausible mechanism for an acid-catalysed isomerisation of the type exhibited above has been proposed as taking the form (440) to (441). Dehydration of 2-methylperinaphthanol gave a methylperinaphthene formulated as (439) on the basis of catalytic hydrogenation to the known 2-methylperinaphthane. In so far as isomerisation was not evidenced in this example, it would appear to be the most stable isomer of the alternative 2, 5 and 8 series.



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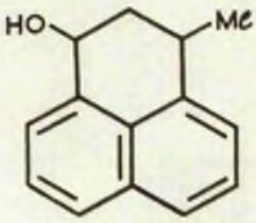

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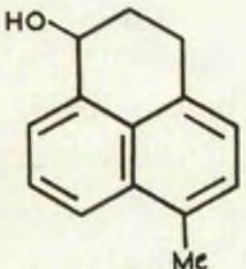

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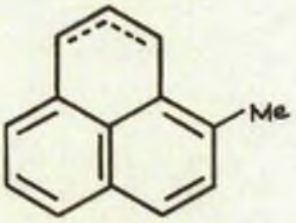
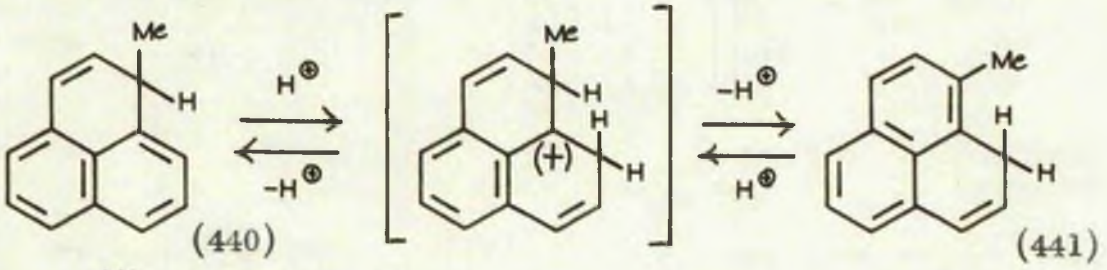


(438)

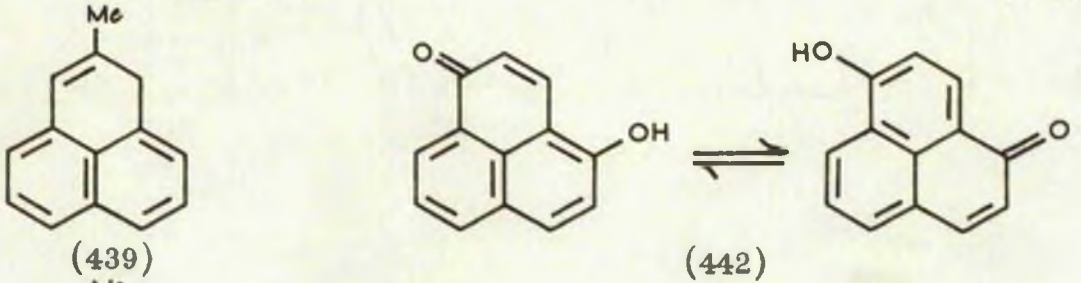
Attempted isomerisation of the methylperinaphthene (438) obtained from the first series of dehydrations, or of 2-methylperinaphthene (439) by conversion to the respective lithio derivatives

followed by hydrolysis gave only the starting material in high yield. Though base-catalysed isomerisation has thus not been demonstrated for the perinaphthene series, there would appear to be no fundamental reason why this should be so. Methylation of perinaphthene by interaction with phenyl lithium followed by methyl iodide resulted in the production of a methylperinaphthene identical with (438), although no acid was involved in the reaction. Treatment of 2-methylperinaphthene (439) with excess of the above reagent gave rise, on the absorption of two moles of methyl iodide, to the production of a dimethylated derivative. The latter resisted further methylation and did not yield a red lithio salt, on which basis a gem dimethyl group was assigned to the molecule. Synthetic and degradative experiments have established that the gem dimethyl group is in position 6 (443) with respect to the original 2-methylperinaphthene[296].

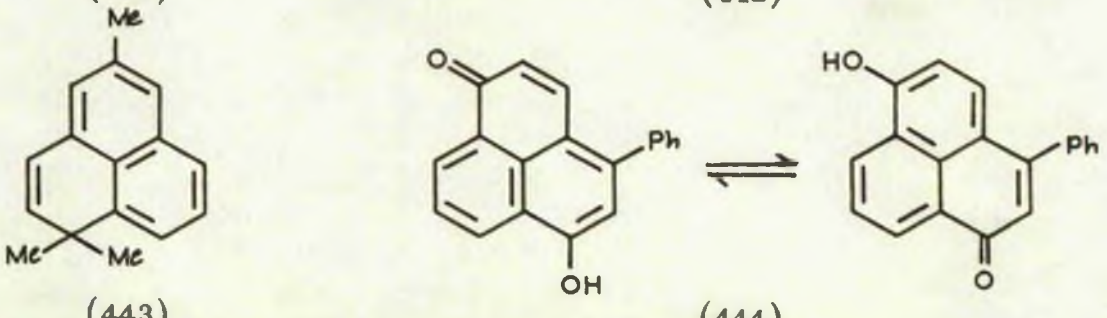
The two isomeric hydroxyperinaphthenones (442) and (444) have recently been synthesised. Tautomeric potentialities in these compounds, portrayed below, have been realised in that each gives two isomeric ethers on O-methylation[308].



(440) (441)



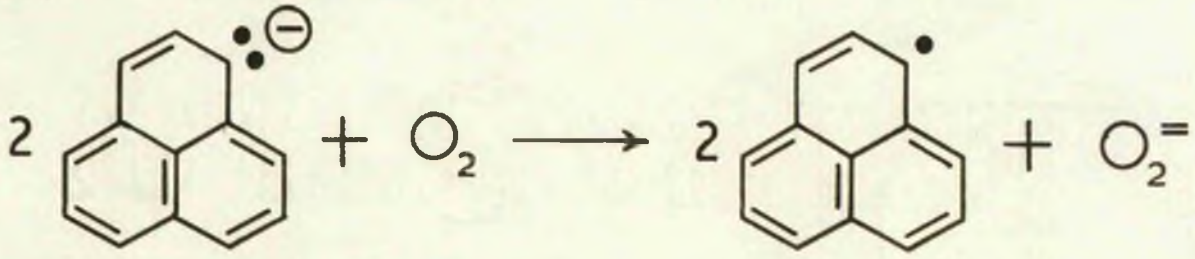
(439) (442)



(443) (444)

A,IV,8. The Anion, Radical and Cation derived from Perinaphthene.

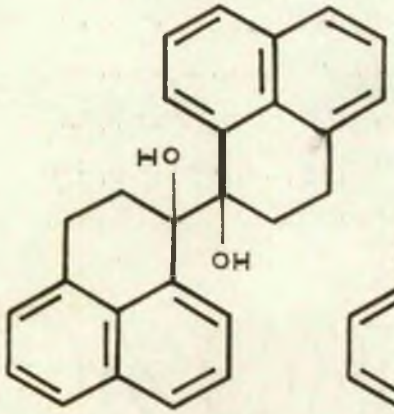
It has already been indicated that the red perinaphthenide anion may be obtained as its lithic or potassic derivative. In this connection it was observed that, on application of the Vanschiedt test which involves formation of the anion, a blue-green colour developed. In addition, a similar colour resulted on the attempted dehydrobromination of perinaphthene dibromide, on treatment of perinaphthene with N-bromsuccinimide and also with triphenylmethyl. Furthermore, such a colour was observed when, in an attempt to prepare 1-bromoperinaphthene as a possible route to the perinaphthenyl radical, 6-bromoperinaphthanol was subjected to dehydration using ethanolic hydrogen chloride[295].



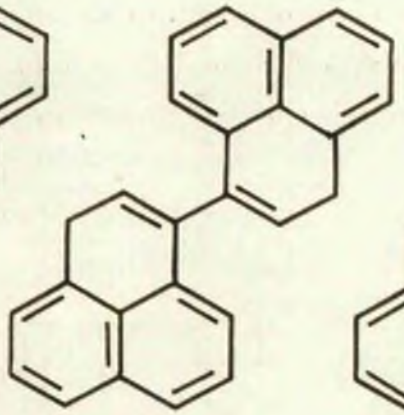
(318) (317)

It has now been shown that such a colour is produced rapidly when ethanolic/ethereal solutions of the red potassium perinaphthenide are exposed to atmospheric oxygen. That the entity responsible for colour development in this case and in the instances detailed above is the hitherto unknown perinaphthenyl radical (317) has been shown by the isolation of the latter as a green thermally unstable solid. The radical is completely converted at room temperature, in an atmosphere of oxygen, to a green heat sensitive solid, which may be thermally decomposed in vacuo to a mixture of peropyrene (418) and perinaphthenone. The speed of this secondary reaction is sufficiently attenuated so as to permit the preparation of the radical in quantity by direct oxygenation of a solution of the perinaphthenide anion (318) followed by hydrolysis and working-up of the organic phase. A spontaneous one-electron transfer from anion to molecular oxygen is visualised, as

in (318) to (317), and in support of this quantitative peroxide anion formation has been demonstrated. Perinaphthenyl itself undergoes ready transformation on heating, e.g. in boiling benzene, to peropyrene (418). The presence of a highly delocalised system is reflected in the failure of this radical to react with nitric oxide.



(445)



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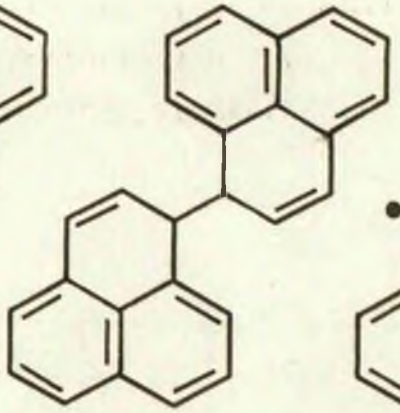

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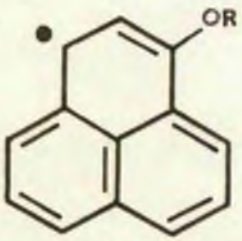
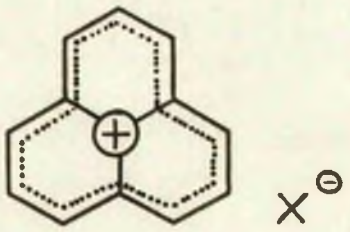


(448)

In addition to the irreversible removal of perinaphthenyl by subsequent oxidation, reversible dimerisation has been demonstrated. Thus the bimolecular reduction product (445), obtained by treatment of perinaphthanone with amalgamated aluminium in anhydrous ethanol/benzene, gave on addition to propionic acid containing a catalytic quantity of hydrogen chloride perinaphthenyl immediately. The course of the reaction is portrayed as involving acid-catalysed prototropy of the initial dehydration product (446) to (447), followed by spontaneous fission of the carbon-carbon bond joining the two perinaphthenyl radicals. The ready formation of the perinaphthenyl radical as a result of the processes detailed above is in conformity with the ease of reversible one-electron addition observed in the polarographic reduction of perinaphthenone[297].

Three simple derivatives of the perinaphthenyl radical are known. Thus treatment of an ethereal solution of perinaphthenone with

acetyl or benzyl chloride, followed by reduction with zinc, or better activated magnesium, resulted in the production of a deep blue colouration, presumed to be due to the presence of acetyloxy or benzyloxy radicals respectively (448; R = CH_3CO- or C_6H_5CO-). On chromatography of a solution of perinaphthenone in methanol which has been treated with anhydrous hydrogen chloride, the eluates have been observed to possess a deep blue colouration believed to be due to methoxyperinaphthenyl (448; R = CH_3). Attempts to isolate solid products from the above resulted in the formation of polymeric material (cf. thermal decomposition of perinaphthenyl[298]. Apart from the unsuccessful attempt to prepare the parent radical from a bromoperinaphthene described earlier, the existence of this entity has been claimed in a solution of perinaphthene in carbon tetrachloride which has been sealed off in air and stored for several months. The electron spin resonance spectrums of perinaphthenyl has been reported on the basis of determinations made with this solution[311]. Perusal of the preceding manuscript on the properties of the authentic radical sheds considerable doubt on the possibility of the presence of the latter under the conditions specified.



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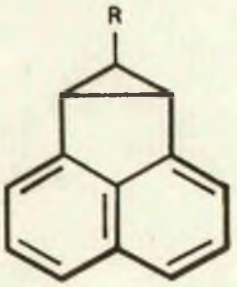

(450)

Interaction of perinaphthenyl with iodine gives a salt-like compound whose analysis indicates a stoichometry corresponding to perinaphthenylium iodide (449; X=I)[297]. Independently, treatment of acenaphthylene with diazoacetic ester gave an ester (450; R= COOEt), which was converted by standard procedures to the chloride (450; R= Cl). Although possessing no ionic properties, on interaction with silver

perchlorate a yellow substance was obtained which doubtless involves the perinaphthenylium cation (449; X= ClO_4)[299]. Both these compounds dissolve only in polar organic solvents, e.g. nitromethane, and are precipitated by non-polar solvents. The existence of perinaphthenylium salts has, of course, been foreshadowed by numerous properties detailed earlier in connection with perinaphthenone, and is in analogy with the tropylium salts derived from tropone.

The description of the successful isolation of the perinaphthenide anion, the perinaphthenyl radical and the perinaphthenylium cation satisfactorily brings to a conclusion the evidence which has been cited in support of these entities, whose postulated existence was outlined in (A,III,8). The ready convertability of anion to radical, and the subsequent conversion of radical to cation would seem to indicate a corresponding order of increasing stability. Greater stability is intuitively associated with delocalised π-electron systems in which the number of mobile electrons and carbon atoms involved are the same(c.f. benzenoid hydrocarbons and azulene). The greater stability of the cation is thus in accordance with expectation. Perinaphthene is unique amongst the aromatic carbocyclic series in that significant delocalisation energy is invested in three discrete oxidation states (c.f. cyclopentadiene and cycloheptatriene). Though thus far only the transformation of anion to cation has been demonstrated, there would appear to be no fundamental reason why the converse should not be possible. It is interesting to note that the mobile electron systems in the radical and cation do not conform to Hückel's Rule.

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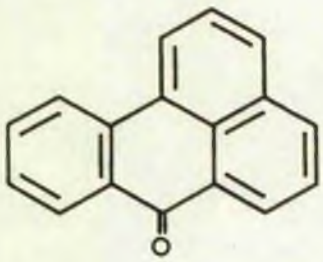
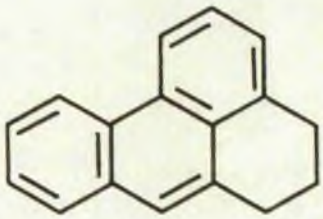
A,IV,9. Other Peri-condensed Systems.

It is of some interest to enquire whether the ring homologues of perinaphthene show properties which are in any degree in alignment with those of the parent systems. Unfortunately ring annelation results in a considerable modification in properties, but at least in two examples there is some evidence that the characteristics of perinaphthene

survive.



(451)



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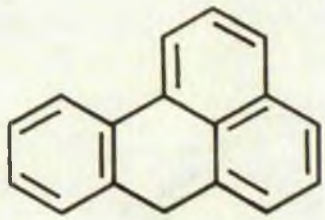


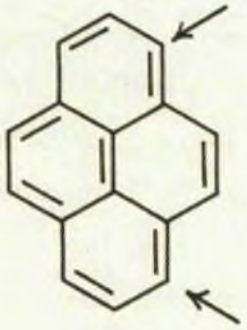
(453)

Benzanthrone (451) or 2:3-benzperinaphthenone, the ketone derived from benzanthrene, or 2:3-benzperinaphthene, is a compound which has been of considerable interest in dyestuffs chemistry, and consequently numerous synthesis have been elaborated for it[300]. It does not have a basicity of the order of perinaphthenone, dissolving only in concentrated sulphuric acid, but electrophilic substitution does take place in the perinaphthene moiety at the 1 position. This can be interpreted in terms of the greater polarisability of the latter, or alternatively of the greater stabilisation of the transition state through the delocalisation energy obtaining in the perinaphthenylium cation. In analogy with the perinaphthene series, 1:4 addition of Grignard reagents to (451) has been demonstrated[301].

Reduction of (451) with red phosphorus and hydrogen iodide has been shown to give 1:10-trimethylene phenanthrene (452)[302], a reaction which parallels an identical reduction of perinaphthenone itself. The most interesting property involves the reduction of (451) with aluminium isopropoxide to give benzanthrene (453) in about 50% yield[303], a process in conformity with the action of lithium aluminium hydride on the perinaphthenone series. The compound (453) itself has not been widely investigated, though it is slowly air oxidised to (451). It would be expected to possess potentialities for anion and radical formation, though this has thus far not been demonstrated.

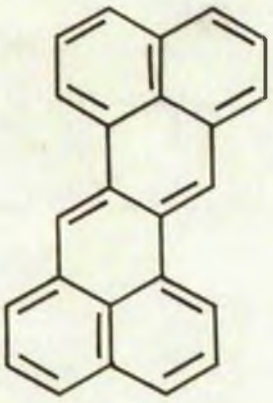
The well known hydrocarbon pyrene (454) results from peri fusion of a benzene ring on to perinaphthene. Though an extremely stable

compound characteristic of the benzenoid series, in one aspect of its reactions reference may be made to the latent influence of the former moiety. Electrophilic substitution takes place at the 1 position on the pyrene nucleus and successive polysubstitution involves the 6, 8,



(454)

and 3 positions. Likewise oxidation by chromic acid gives the 1:6 and 1:8 quinones[265]. A suggestion has been made that these positions owe their reactivity to the fact that they are situated at the terminal sites of a triene system shown in (454)[304]. In the light of knowledge derived from a consideration of the perinaphthene system it would seem more satisfactory to interpret these phenomena in terms of a transition state involving the perinaphthenylium cation.



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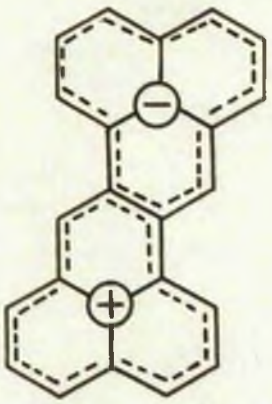

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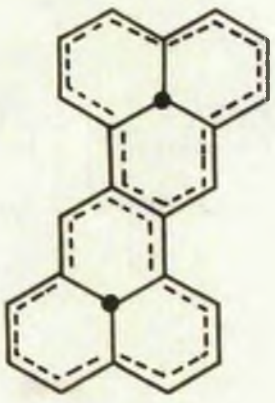

(457)

The molecule formed by the fusion of the two perinaphthene molecules has been termed zethrene (455) on account of its z-like shape. Though originally identified as a highly basic, green, stable solid[305], this description has been shown to be erroneous by the preparation of a more authentic compound by a somewhat long synthesis involving chrysene, and its isolation from a number of simple reactions[306]. Thus zethrene has been obtained in very low yield by passing acenaphthene vapour over an industrial dehydrogenating catalyst - 'kali-chemie'. It is also obtained together with a number of other hydrocarbons when acenaphthene is refluxed over a glowing yellow filament. Finally it has been isolated from a melt consisting of sodium chloride and aluminium chloride together with either acenaphthene or acenaphthylene.

From the foregoing account of perinaphthene, dipolar (456) or diradical (457) structures for zethrene would seem to be equally possible, and some stabilisation of the molecule might be expected on account of them. Contrariwise, zethrene may equally well be regarded as a dibenz-chrysene or a dibenztetracene. The observed properties seem to approximate more closely to the latter, for (455) is an unstable red solid which undergoes photo-oxidation by the action of light and gives a colourless adduct with maleic anhydride. Molecular orbital calculations have indicated a structure which may be portrayed as two naphthalene units joined by a butadiene system[312].

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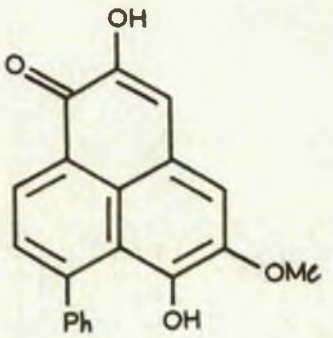
A.IV.10. Natural occurence of the Perinaphthene Ring System.

The occurence in nature of compounds containing the perinaphthene ring system has been recorded only recently, though its existence in natural products is to be expected in view of the stability of the system. Thus Cooke and Segal(1955)[307][308] have isolated a red crystalline glycoside from the bulbous roots of Haemodorum corymbosum Vahl, the aglycone of which appeared to be a polycyclic enolic α-diketone. Further investigation has indicated that the aglycone is a dihydroxy-methoxyphenylperinaphthene based on the 2-hydroxyperinaphthan-1-one

skeleton, and formula (458) represents one of three possibilities. The tautomeric potentialities of such a structure have been confirmed by synthesis of simpler derivatives described in (A,IV,6).

Likewise the fungal pigments herqueinone and norherqueinone, isolated from Penicillium herquei, and atrovenetin(identical with desoxynorherqueinone obtained by reduction of norherqueinone with zinc and acetic acid) have been shown to be derivatives of 9-hydroxy-perinaphthenone (430). Herqueinone on acid hydrolysis gives methyl isopropyl ketone and Xanthoherquein, and preliminary investigations have indicated the presence of two oxygen atoms as in (430), four phenolic hydroxyls and one ($C-CH_3$) group[309][316].



(458)

PART A: LITERATURE CITED.

Abbreviations used.

Anal. Chem.	Analytical Chemistry.
Anal. Real.Soc. Espan.	Analee de la real Sociedad espanola de Fisica y Quimica.
Angew. Chem.	Angewandte Chemie.
Ann.	Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie.
Arom. Kohl.	Aromatische Kohlenwasserstoffe, 2nd., Edn., (Berlin, 1952).
Atti Acad. Lincei	Atti della Academia nazionale dei Lincei.
Aust. J. Chem.	Australian Journal of Chemistry.
Aust. J. Sci.	Australian Journal of Science.
Ber.	Berichte der deutschen chemischen Gesellschaft (discontinued with vol. 77, 1944; continued as Chemische Berichte with vol. 80, 1947).
Biochem J.	Biochemical Journal.
Bull. Acad. Sci.	Bulletin de l'Academie des Sciences de l'U.R.S.S. (subtitle used formerly for Izvestiya Akademii Nauk S.S.S.R.).
Bull. Soc.	Bulletin de la Societe chimique de France.
Bull. Soc. Jap.	Bulletin of the Chemical Society of Japan.
C.R.	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences.
C.R. Trav. Lab. Carl.	Comptes rendus des Travaux du Laboratoire de Carlsberg.
Chem. Ind.	Chemistry and Industry.
Chem. Obz.	Chemicky Obzor.
Chem. Rev.	Chemical Reviews.
D.R.P.	Deutsche Reichspatente.
Dok. Akad. Nauk.	Doklady Akademii Nauk S.S.S.R.
Exp.	Experientia.
Helv. Chim. Acta.	Helvetica Chimica Acta.

J.A.C.S.	Journal of the American Chemical Society.
J.C.S.	Journal of the Chemical Society.
J.C.S. Jap.	Journal of the Chemical Society of Japan.
J. Ch. Phys.	Journal of Chemical Physics.
J. Chim. Phys.	Journal de Chimie Physique.
J. Gen. Chem.	Journal of General Chemistry (U.S.S.R.), New York. (U.S. Translation of Zhurnal obshchei Khimii).
J. Org. Chem.	Journal of Organic Chemistry.
J. Pr. Chem.	Journal für praktische Chemie (discontinued after vol. 162, 1943).
K.D.V.S.	Kongelige danske Videnskabernes Selskab, Mathematisk-Fysiske Meddelelser.
Nature.	Nature.
Mon.	Monatshefte für Chemie.
Phil. Mag.	Philosophical Magazine.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
P.K.A.W.A.	Proceedings, koninklijke nederlandsche Akademie van Wetenschappen, Amsterdam.
Proc. Jap. Acad.	Proceedings of the Japan Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. Rev.	Quarterly Reviews.
Ric. Sci.	Ricerca scientifica.
Spect. Acta.	Spectrochimica Acta.
Trans. Far. Soc.	Transactions of the Faraday Society.
Z. Anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Natur.	Zeitschrift für Naturforschung.
Z. Physik.	Zeitschrift für Physik.

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PART B.

NOTES.

Where original literature is cited, this is indicated by numbers in parentheses and superscript, a key to which will be found at the end of part B.

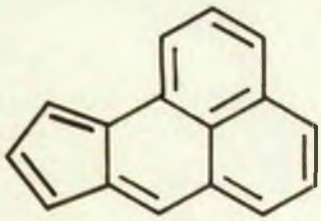
Infra-red spectral measurements, which are recorded in part B, were conducted and interpreted by M. St.C. Flett (I.C.I., Manchester). As only certain absorption maxima are of relevence, the entire spectrographs have not been reproduced in this work, nor have the values been quoted again in part C.

Unless otherwise stated, acid concentrations are expressed in terms of a percentage weight in weight (% w/w).

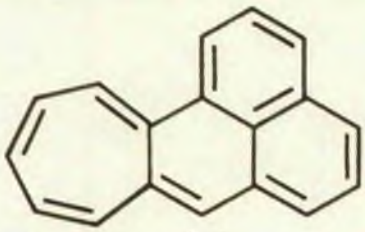
The terms light petrol and petrol refer respectively to those solvents more commonly designated as petroleum ether (b.p. 40-60°) and petroleum ether (b.p. 60-80°).

B.I. INDENO[2,1-a]PERINAPHTHENE.

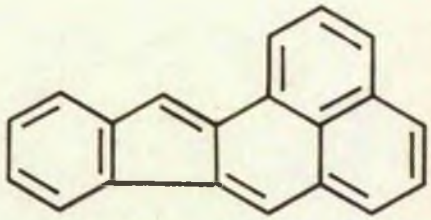
B.I.1. Indeno[2,1-a]perinaphthene: Synthesis.



(1)



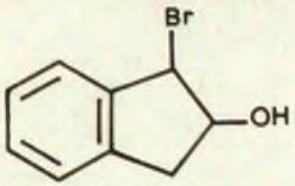
(2)



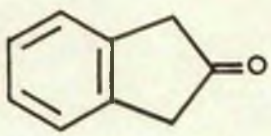
(3)

For reasons expounded in detail in (A,III,8.), considerable interest attaches to the synthesis of cyclopenta[a]perinaphthene (1) and cyclohepta[a]perinaphthene (2). Compounds containing either of these ring systems were hitherto unknown, and this fact prompted an attempt to synthesise, in the first instance, a ring homologue of (1), indeno[2,1-a]perinaphthene (3). The successful outcome of this attempt is reported in the foregoing.

In view of the instability of perinaphthene and the difficulties associated with the preparation of suitable substituted derivatives, a synthesis was sought whose ultimate step would afford the fully aromatised perinaphthene directly from a precursor whose molecule did not possess this ring system. The most satisfactory synthesis of perinaphthenone involves the cyclodehydration of the corresponding oxymethylene compound in acid media (A,IV,2). It seemed appropriate, therefore, to emulate this synthesis insofar as was possible by the nature of the desired product. Thus the primary problem entailed the synthesis of a suitable oxymethylene derivative.

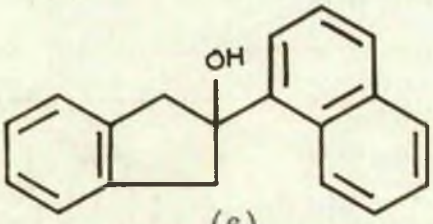


(4)

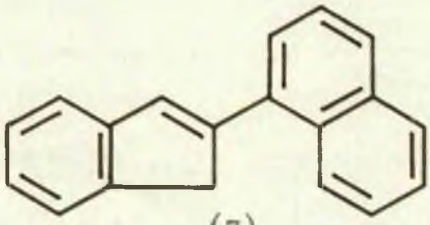


(5)

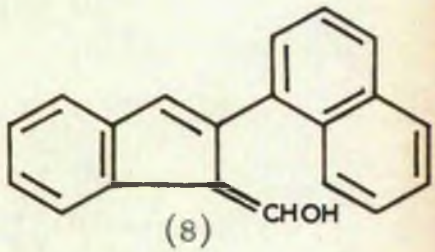
2-Bromo-1-hydroxyindane (4) is readily obtained on treatment of indene with a solution of bromine in aqueous potassium bromide (C,I,1). This compound may be dehydrobrominated using aqueous:alcoholic potassium hydroxide to give 2-hydrindone (5). In view of the considerable readiness of the resulting ketone (5) to undergo condensation type reactions, unless the original reaction mixture is maintained in a slightly acid condition, yields are liable to be poor. The product (5) crystallises in long colourless needles when pure, but deteriorates to a yellow oil in a matter of a few days, from which up to 80% of pure ketone may be recovered by steam distillation. On account of the above, 2-hydrindone (5) is best prepared immediately before use.



(6)



(7)

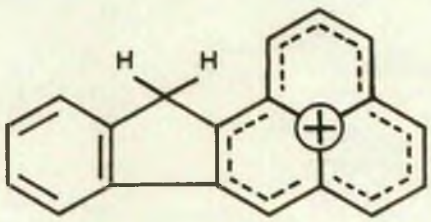


(8)

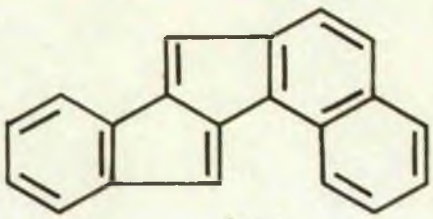
Interaction of (5) with α-naphthyl magnesium bromide gave an orange-coloured oil containing the expected carbinol (6) together with its dehydration product (7) and a considerable amount of naphthalene. The latter was successfully removed by steam distillation, whereupon the former mixture was completely dehydrated in a boiling formic:acetic acid mixture. The resultant 1-2'-indenylnaphthalene (7) displayed monotropy, and the metastable modification tended to crystallise from impure solutions. The pale yellow oil from the dehydration reaction was processed in the usual manner, and then subjected to filtration on alumina in light petrol:benzene solution (8:1). From the almost colourless eluates the hydrocarbon (7) was deposited as colourless needles which melted at 77-79° on one crystallisation from light petrol. The melt was observed to solidify at 81-84° in the form of a mass of colourless plates which eventually melted at 90-91°. Contrariwise, on distillation of the yellow oil (above) prior to filtration

through a column of alumina, the hydrocarbon (7) was obtained directly in the form of colourless plates, m.p. 90.5-91°, by crystallisation from the eluates. The product (7) was characterised by the preparation of the sym-trinitrobenzene complex, which crystallised in the form of orange coloured plates from ethanol.

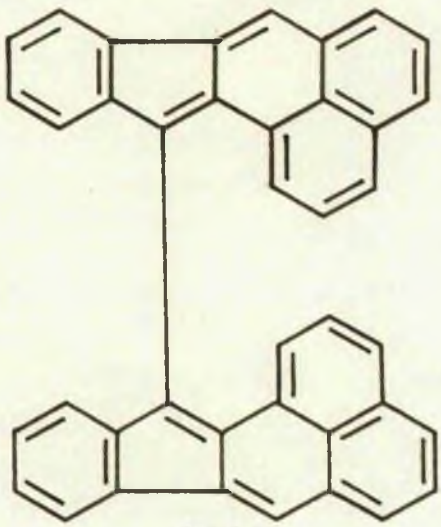
Conversion of the hydrocarbon (7) to the corresponding oxymethylene derivative (8) was accomplished in good yield by condensation of the latter with ethyl formate in the presence of anhydrous potassium methoxide. The product (8), which was an unstable red oil, did not crystallise, and proved insufficiently stable to withstand distillation. Consistently with its tautomeric nature, however, it formed both a benzoate, which crystallised in the form of yellow prisms from acetic acid, and a 2:4-dinitrophenylhydrazone, which crystallised in the form of orange-red prisms from propionic acid. In practice it was found expedient to conduct the preparation of the oxymethylene derivative with as much haste as possible, and to treat the crude product immediately in accordance with the next step in the reaction sequence.



(9)



(11)



(10)

Attempted cyclodehydration of (8) using respectively hydrogen bromide in acetic acid, phosphorus pentoxide in benzene, polyphosphoric

acid and anhydrous liquid hydrogen fluoride was without positive outcome. Ultimately, cyclisation by the use of 93% sulphuric acid was shown to give a brown residue from which could be extracted, in low yield, a highly coloured, benzene soluble substance.

Considerable delocalisation energy is associated with the perinaphthenylium cation (316; A,III,8), and indeno[2,1-a]perinaphthene (3) should be basic in character on account of the stabilisation of the conjugate acid (9) through the former entity. In conformity with this, it was observed that the highly coloured substance was partially soluble in sulphuric acid of concentrations as low as 64% to give an intensely green-coloured solution, and accordingly complete extraction was carried out from the benzene solution using 77% sulphuric acid. Regeneration of the organic material by dilution of the acid with an excess of water gave a compound whose solution in benzene was coloured bright red. On chromatography on alumina of the above solution, followed by concentration of the eluates, a product crystallised in the form of reddish-brown leaflets which was subsequently shown to be indeno[2,1-a]perinaphthene(3). This hydrocarbon (3), the sym-trinitrobenzene complex of which crystallised in the form of black needles from ethanol, was obtained in a maximum yield of 7.8% only (with respect to weight of indenylnaphthalene used).

The acid insoluble fraction of the cyclodehydration product was subjected to controlled chromatography on alumina utilising its solution in benzene:light petrol mixture. The eluates were carefully concentrated by evaporation which resulted in a homogeneous product being deposited in the form of small purple-black prisms. This compound, also a hydrocarbon, possessed almost the same empirical formula as (3), but gave no complex with the usual complexing agents. Its formulation as di(indeno[2,1-a]perinaphthen-12-yl) (10) has been adduced on suggestive evidence only.

Conditions during cyclodehydration for the attainment of optimum yields proved extremely critical, and variations within only very narrow

limits were permissable. Thus it was found that the acid cyclising medium was only effective if its strength lay between 89% and 95%, and the yields deteriorated sharply on either side of 93%. The most satisfactory period of exposure of the oxymethylene derivative to the sulphuric acid mixture was found to be between 45 and 90 seconds, but if the former was prolonged beyond 2 minutes, no useful material could be isolated from the resultant product. Reproducible results were only obtained when (3) was dissolved in an excess of dry benzene (ca. 10gm. in 200ml.) prior to cyclisation, though occasionally yields of a high order were obtained using very much less solvent (20ml.). It was quite frequently observed, however, that under the latter conditions the product consisted of (10) to the exclusion of (3). During the cyclisation reaction, there was only a very small spontaneous increase in temperature. Though it was found advantageous to conduct this operation having previously warmed the benzene solution to 50°, the temperature proved to be the least important factor in influencing the yield of (3)(for experimental see C,I,5).

It will be apparent from the rationale of the above reaction sequence that it does not lead unequivocally to one product, and depending on whether ring closure at the final stage takes place at position 2 or 8 on the naphthalene nucleus, benzo[a]naphtho[1,2-a]-pentalene (11) or indeno[2,1-a]perinaphthene (3) results respectively. The isolation of two products might seem to be in conformity with the deduction that both modes of cyclisation had actually taken place. Persual of (A,III,5), where the properties of the closely related 1:2-4:5-dibenzopentalene (181; A,III,5), are detailed indicates that (11) would probably be insufficiently stable to withstand the reaction conditions involving the use of strong acid. There is, however, preliminary evidence which supports the notion that this material is a dimerised form (10) of (3). Unfortunately accurate molecular weight determinations, either by the Rast or by crystallographic methods, which would be of primary importance in assessing the validity of this

suggestion, have proved impossible on account of the colour density and size of crystals respectively. An approximate molecular weight determination by the former method has indicated a value of 381 ($C_{40}H_{12}$ = 503).

In contrast, the formulation of the basic component of the reaction product as indeno[2,1-a]perinaphthene (3) would seem reasonable, and has been established beyond doubt by further synthetic work.

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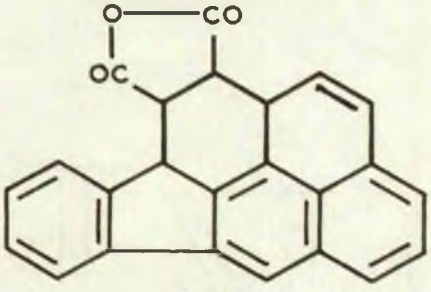
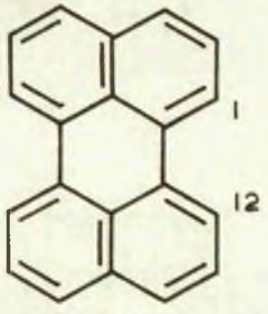
B,I,2. Action of Dienophiles on Indeno[2,1-a]perinaphthene: First Synthesis of Indeno[1,2,3-cd]pyrene.



(12)

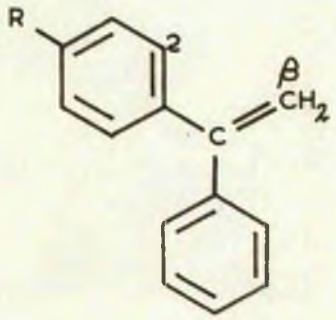


(13)

Early investigations into the properties of indeno[2,1-a]perinaphthene (3) revealed a reactivity towards dienophiles. Thus treatment of (3) with maleic anhydride in non-oxidising media (boiling acetic acid:xylene solution) resulted in the formation of an adduct in almost quantitative yield whose formula has been shown to be 10b:11:12:12a-tetrahydro-indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride (12) (for experimental see C,II,1 et seq.,).

Examples of the Diels Alder reaction where both multiple bonds are supplied by an aromatic system are confined to the acene series[1] on the one hand, and perylene (13)[2][3] and certain of its ring homologues on the other. In the former case, the resultant adduct involves a tricyclic system and subsequent aromatisation is impossible

on stereochemical grounds. With perylene (13), however, the tetrahydro-adduct appears to be unstable, and addition only takes place at the 1 and 12 positions by continuous conversion of the primary adduct to the fully aromatised derivative, which is achieved by carrying out the reaction in oxidising media. No primary adduct has been isolated from perylene (13) or any of its homologues. As a consequence, the ready formation of (12) described above must be regarded as unique for this type of compound.



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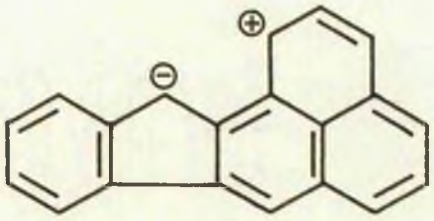
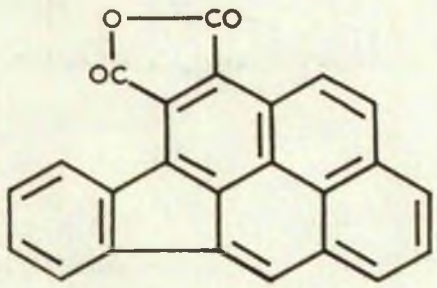


(15)

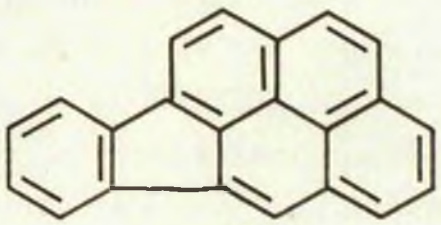
Though the exact mechanism of the Diels Alder reaction has not been elucidated, both biradical and ionic processes have been proposed, and there is evidence in support of the latter. Thus it has been shown that the tendency of maleic anhydride to add to styrene is influenced by substitution in the para but not the meta position in the benzene ring, electron releasing substituents promoting addition[4]. Furthermore, investigation of para-substituted 1:1-diarylethylenes (14), with a view to determining the effects of various substituents on the two possible modes of addition, has revealed the necessity of an enhanced electron density at the β position coupled with a corresponding positive charge at the 2 position to ensure maleic anhydride addition involving the substituted ring[5]. Support from the latter has been obtained by the use of unsymmetrical dienophiles[6]. If the polar mechanism is accepted, the addition of maleic anhydride to (3) can be interpreted in terms of the ready polarisability of the indeno[2,1-a]perinaphthene structure to

give a form of the type (15) which is in conformity with the known stability of the charged entities involved, and with the proposed reacting state of this compound (A,IV,8 and A,III,8).

Irrespective of the ultimate mechanism of the addition process, the energy required before reaction can take place is of the order of that involved in the localisation of the two π-electrons at the sites of addition; the so-called para-localisation energy[7]. Though two new σ bonds are formed, the energy associated with the delocalised electron system of the primary adduct cannot be far removed from that obtaining in the transition state. As an extension the ready isolation of a primary adduct, as opposed to the fully aromatised derivative, would seem to indicate that the difference in energy between the π-electron structures of the diene component and the resulting product is not great. As applied in this particular context, it must be concluded that the energy difference between the appropriate systems in indeno[2,1-a]perinaphthene (3) and the vinyl benzofluorene residue in (12) is small.



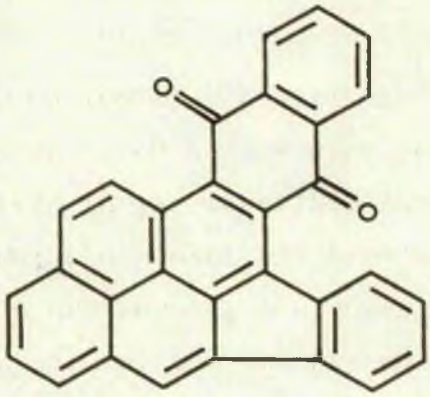
(16)



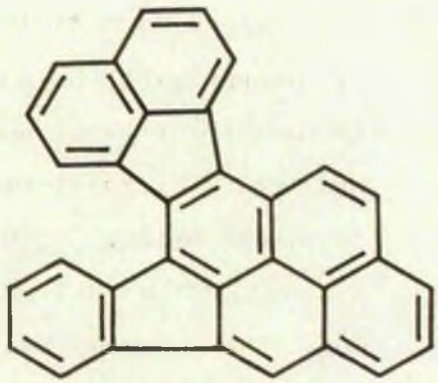
(17)

The tetrahydro-adduct (12) readily underwent dehydrogenation in boiling nitrobenzene to give indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride (16). Alternatively, (16) could be obtained directly by interaction of maleic anhydride and (3) using boiling nitrobenzene as solvent. Finally, (16) was subjected to decarboxylation by pyrolysis with an excess of soda lime, whence indeno[1,2,3-cd]pyrene (17) distilled out of the reaction mixture, and was obtained in the form of bright yellow plates by crystallisation from light petrol:benzene

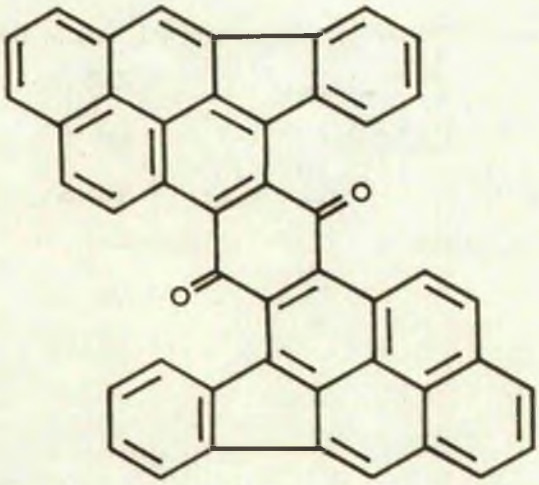
mixture. Structural proof of the formulae assigned to all the above compounds rests on an independent synthesis of (17) from pyrene.



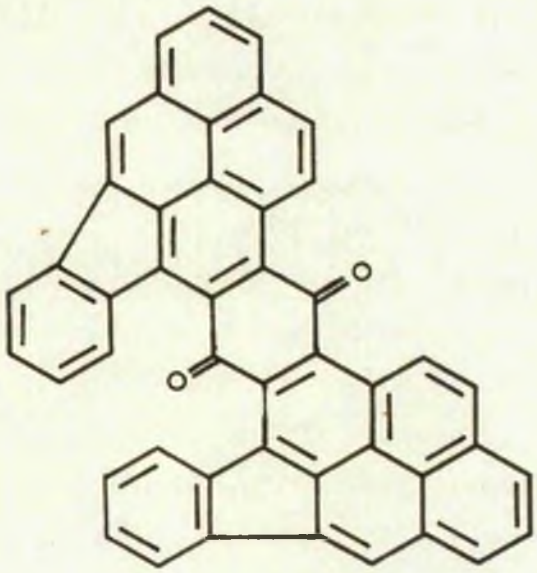
(18)



(20a)



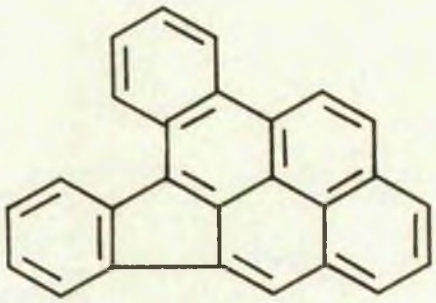
(19a)



(19b)

Preliminary experiments have indicated that indeno[2,1-a]perinaphthene (3) displays diene reactivity towards a number of other dienophiles. Thus with 1:4-naphthaquinone in boiling nitrobenzene it affords the expected tetracene derivative (18). In accordance with its formulation as a quinone, the latter gave a greenish-blue vat with alkaline sodium dithionite. With 1:4-benzoquinone in boiling nitrobenzene

a high melting orange microcrystalline solid was obtained which must possess either of the two potential structures (19a) or (19b). This compound, which gave no vat with alkaline sodium dithionite, is remarkable in that its molecule contains 13 fused rings.



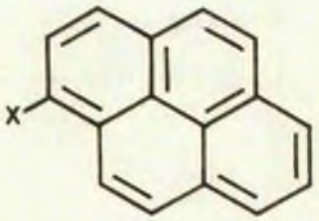
(20b)

An adduct, to which has been ascribed the structure (20a), was obtained on treatment of (3) with 9-bromoacenaphthylene in boiling nitrobenzene. This is believed to be a unique example of the latter reagent acting as a dienophile. Furthermore, benzyne addition to indeno[2,1-a]perinaphthene has been demonstrated, and the adduct has been assigned the formula (20b) by analogy with the formation of (16).

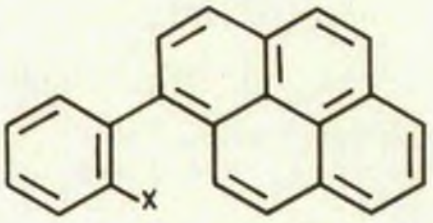
.....

B,I,3. Indeno[1,2,3-cd]pyrene: Synthesis from Pyrene.

As a consequence of the ambiguity obtaining in the synthesis of indeno[2,1-a]perinaphthene, it seemed appropriate to resolve the problem by obtaining evidence in connection with the Diels Alder addition reaction. Accordingly, an independent synthesis of indeno[1,2,3-cd]pyrene from pyrene was initiated.



(21)



(22)

Pyrene undergoes electrophilic substitution in the 1 position[8], and 1-nitropyrene (21; X = NO_2) may be readily obtained by subjecting the former to standard nitration procedure utilising a nitric:acetic acid mixture. The latter affords 1-aminopyrene (21; X = NH_2) on reduction with sodium hydrosulphide. Conversion to the iodo-compound (21; X = I) may be achieved in somewhat low yield by treatment of the corresponding diazonium sulphate (21; X = $N_2^+.\frac{1}{2}SO_4^-$) with potassium iodide followed by copper powder[9].

A crossed Ullmann reaction was conducted between 1-iodopyrene (21; X = I) and o-bromonitrobenzene by heating the reactants at about 210° in the presence of an excess of copper bronze during the course of 3 hours. The desired product (22; X = NO_2) was isolated from the resultant mixture by controlled chromatography. Thus by careful elution of the latter from a column of alumina using gradually increasing proportions of benzene in a benzene:light petrol mixture, almost complete separation was achieved, and 1-(o-nitrophenyl)pyrene (22; X = NO_2) was obtained in the form of golden-yellow needles in a yield of 44%. Catalytic hydrogenation of (22; X = NO_2), using either 20% palladised charcoal in acetic acid or Raney nickel in ethanol, afforded the corresponding amino- derivative (22; X = NH_2) as a somewhat unstable brown oil which did not crystallise, but which was characterised by the formation of its picrate.

The amine (22; X = NH_2) was subjected to a Pschorr-type procedure. Thus the corresponding diazonium sulphate (22; X = $N_2^+.\frac{1}{2}SO_4^-$) was treated with copper bronze at 100° which resulted in the formation of

indeno[1,2,3-cd]pyrene (17) in 53% yield. The m.p. of this compound was not depressed on admixture with the product (17) obtained by the reaction sequence outlined in (B,I,2), and the absorption spectra of the two were superimposable. The visible and ultra-violet absorption spectra of indeno[2,1-a]perinaphthene (3) and indeno[1,2,3-cd]pyrene (17) are combined on plate III for comparison. The two spectra show considerable correspondence in the number and intensities of band groups and maxima, though the maxima of the former lie at longer wavelengths.

Though in the cyclisation procedures described in (B,I,1) and (B,I,3) two modes of ring closure are at all events theoretically possible, the production of identical compounds in (B,I,2) and (B,I,3) can only be accounted for if cyclodehydration of the oxymethylene derivative (8) results in the formation of a six-membered ring and the Pschorr synthesis results in the formation of a five-membered ring. The assignment of the indeno[2,1-a]perinaphthene (3) and indeno[1,2,3-cd]pyrene (17) structures to the products of the former and latter reactions respectively is therefore confirmed without ambiguity.

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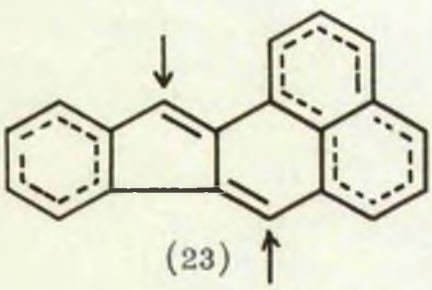
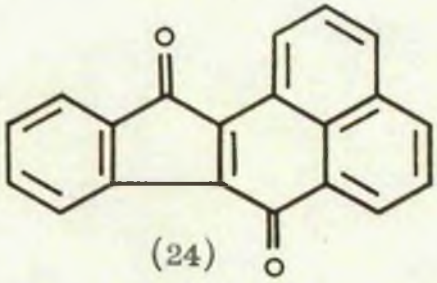
B,II. OXIDATION AND REDUCTION OF INDENO[2,1-a]PERINAPHTHENE.

B,II,1. Oxidation of Indeno[2,1-a]perinaphthene.



(23)



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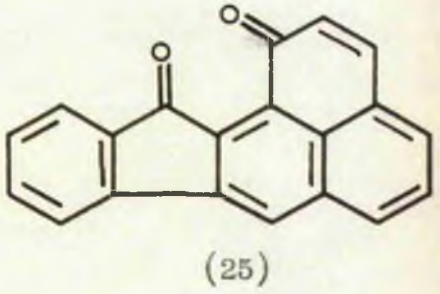

(25)

Examination of the formula of indeno[2,1-a]perinaphthene (3) reveals the occurence of double bonds at positions 7 and 12 in all the possible Kekulé forms (23). As a consequence it was hoped that oxidative attack might occur at the terminal sites of this diene system, and that structural evidence might result from further degradation. Indeno[2,1-a]perinaphthene proved susceptible to oxidation by ozone, but attempted isolation of the product was without positive outcome.

A product was obtained, however, by the oxidation of (3) with chromic anhydride in acetic acid, which has been formulated as a quinone both on the basis of analytical data and the fact that it gives a violet-blue vat on treatment with alkaline sodium dithionite. Following from the preceding observation, it might seem appropriate to assign structure (24) to this quinone. Alternatively, evidence derived from the mode of dienophile addition to (3) suggests structure (25). In agreement with either (24) or (25), infra-red spectral determinations on the quinone in the solid state as a 'Nujol' mull has revealed that the carbonyl stretching frequencies occur at 1704 $cm.^{-1}$ and 1639 $cm.^{-1}$, corresponding to their counterparts in fluorenone (1715$cm.^{-1}$) and perinaphthenone (1637$cm.^{-1}$) respectively. The attempted

formation of a 1:2-diazine derivative, which would be very compelling evidence for the latter, has unfortunately given inconclusive results. The formula of this quinone has not, therefore, been unequivocally established, though it has been demonstrated that the addition of maleic anhydride and the above oxidation have one site in common on the indeno[2,1-a]perinaphthene molecule (B,III,2).

The action of lead tetra-acetate on (3) proved to be of considerable interest. Thus from treatment of the latter in benzene solution with this reagent at room temperature for 1 hour, no trace of the starting material could be detected, but a significant quantity of a product shown to be identical with the non-basic hydrocarbon obtained by the cyclodehydration of the oxymethylene derivative (8) was isolated. In accordance with the proposed formulation of the latter as di(indeno[2,1-a]perinaphthenyl) (10), this reaction must have involved intermolecular dehydrogenation. Intramolecular dehydrogenation under the action of lead tetra-acetate is not unknown[10], but no analagous instance of an intermolecular dehydrogenation by this reagent in the carbocyclic series has been recorded, and the above example must be regarded as unique.

The non-basic hydrocarbon (10) was subjected to the action of lead tetra-acetate under somewhat more forcing conditions. Thus a solution of the latter hydrocarbon in boiling benzene was treated with this reagent over a period of 2 hours, whence a small quantity of green solid was obtained whose analysis corresponded to mono-acetoxy-di(indeno[2,1-a]perinaphthenyl). The full significance of the above observations are invoked in (B,II,3).

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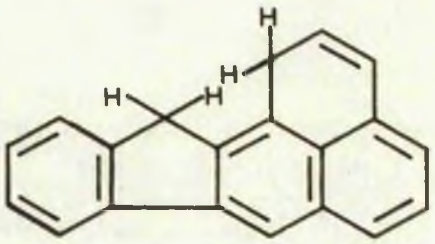
B,II,2. Reduction of Indeno[2,1-a]perinaphthene.

Reduction of aromatic compounds at metal surfaces is believed to take place initially by the dissolution of the metal in a suitable medium to provide solvated electrons in equilibrium with metallic cations. Addition of two electrons to the aromatic molecule yields a mesomeric anion, and the reduction is concluded by the accession of two protons to give a neutral product[11].

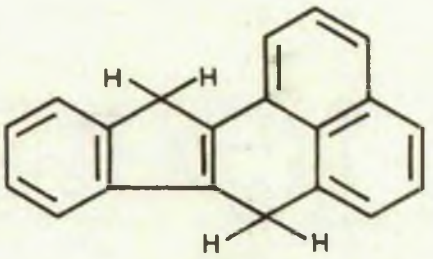
Indeno[2,1-a]perinaphthene might be expected to undergo such a reduction either by a preliminary one- or two-electron process. The delocalisation energy associated at the same time with the cyclopentadienide anion (49; A,II,1) and the perinaphthenyl radical (317; A,III,8) should obtain in the anion-radical formed by fusion of these moieties, and this fact gives cogency to the argument that reduction may proceed initially by the former process. By similar reasoning, of course, a mesomeric di-anion formed by the spontaneous addition of two electrons to (3) would be invested with considerable delocalisation energy, though the lesser stability of the perinaphthenide anion (318; A,III,8) with respect to the corresponding radical as evidence by the ready conversion of the former to the latter (see A,IV,8), renders the preliminary formation of an ion-radical a dintinct possibility. In this context, an investigation of the polarographic reduction of indeno[2,1-a]perinaphthene would be extremely relevent. Irrespective of whether a discrete one-electron process occurs or not, a di-anion will be formed eventually, and the reduction will be consummated by the accession of two protons to the latter; one at position 12, and the other at a suitable site in the perinaphthene moiety.

On treatment with an excess of zinc in boiling acetic acid, indeno[2,1-a]perinaphthene afforded an almost colourless, solid dihydro- derivative, for which formula (26) represents one of a number

of possibilities and the position of the extra hydrogen atom on the perinaphthene nucleus is not known with certainty. A complex from the above was obtained in which two molecules of sym-trinitrobenzene were combined with one molecule of hydrocarbon.



(26)



(27)

Of all the possible dihydro-indeno[2,1-a]perinaphthenes, only one had previously been prepared. Thus it is recorded that interaction of benzyl magnesium chloride with perinaphthan-1-one gave an oil which was subsequently cyclised by the agency of aluminium chloride in carbon disulphide to give (27) in very low yield[24]. Unfortunately in the hands of the author this preparation was without positive outcome.

In order to obtain information as to the structure of dihydro-indeno[2,1-a]perinaphthene, experiments were initiated to locate and degrade the most localised double bond in the molecule. The hydrocarbon proved susceptible to attack by ozone, but no useful material could be isolated from this oxidation.

In the circumstances the use of osmium tetroxide seemed appropriate, Though initially applied as a reagent for the hydroxylation of olefinic double bonds, evidence has accumulated which indicates its suitability for the degradation of the most localised double bonds in polycyclic aromatic systems. Thus it has been shown to hydroxylate the 1:2 bond in pyrene[12], the 9:10 bond in phenanthrene[13], and the 1:2 (and subsequently the 3:4) bond in anthracene[14].

The mode of addition of osmium tetroxide, closely analogous to

the Diels Alder reaction, would seem to be more in alignment with that expected of a double bond reagent than is the case with ozone or diazoacetic ester. Though the latter two reagents interact with naphthalene[15][16] and benzene[17][18], these hydrocarbons are substantially unaffected by the former reagent in conformity with the highly delocalised condition of the double bonds. In addition the superiority of osmium tetroxide over diazoacetic ester has been demonstrated for a specific case[19]. The objection of great toxicity coupled with high cost frequently levelled against this reagent would seem irrelevent.

The outcome of an attempt to hydroxylate dihydro-indeno[2,1-a]-perinaphthene with oxmium tetroxide was somewhat unexpected. It was hoped that the bond corresponding to the 2:3 bond in the perinaphthene moiety would suffer attack, and by further selective degradation furnish a compound of known structure. When a solution of the hydrocarbon in benzene was treated with this reagent in the presence of pyridine, a brown solid separated in the course of 15 minutes at room temperature. Though permitted to stand at room temperature for a prolonged period, the bulk of the precipitate did not increase appreciably in magnitude. The brown residue was not the normal pyridine co-ordination complex of the organo-osmium tetroxide adduct, for it was unaffected by extended treatment with aqueous alkaline mannitol solution. On the other hand, the supernatant organic phase was shown to contain a significant quantity of indeno[2,1-a]perinaphthene, which was extracted with 77% sulphuric acid and regenerated in the manner described elsewhere.

Though the desired product had not been obtained, the novelty of the reaction merited further investigation. In an identical experiment involving perinaphthene, it was observed that two processes were taking place simultaneously. Thus, whereas some of the starting material was consumed in the formation of an adduct from which was eventually isolated

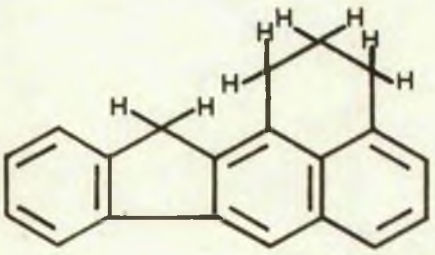
1:2-dihydroxyperinaphthane, the latter reaction was attended with the formation of the perinaphthenyl radical, isolated as perinaphthenylium iodide (A,IV,8)[20]. It would appear, therefore, that osmium tetroxide is acting in the somewhat unusual role of a dehydrogenating agent, and this is doubtless partly a reflexion on the great tendency of dihydro-indeno[2,1-a]perinaphthene to revert to the parent aromatic system, and likewise perinaphthene to revert to the corresponding radical. The occurence of a radical in the latter reaction suggests that it may also exist as an intermediate in the dehydrogenation of the former dihydro-derivative. As an extension, it lends support to the notion that a mesomeric anion-radical features in the metal:acetic acid reduction process of indeno[2,1-a]perinaphthene itself. This instance of osmium tetroxide functioning as a dehydrogenating agent finds no parallel in the chemical literature.

The failure attending the oxidative experiments outlined above prompted attempts to pursue structural investigation by catalytic reduction, though once again the results were somewhat unexpected. When a solution of dihydro-indeno[2,1-a]perinaphthene in acetic acid was exposed to an atmosphere of hydrogen in the presence of 20% palladised charcoal, no uptake of gas was observed, but the initially pale pink solution became deep red. On investigation the chief component of the reaction mixture was found to be indeno[2,1-a]perinaphthene, which was recovered in substantial quantity. No strictly analagous dehydrogenation reaction of so spontaneous a nature has been recorded.

Notwithstanding the above, hydrogenation of this hydrocarbon in acetic acid solution was shown to proceed smoothly in the presence of Adam's platinum oxide catalyst. Unfortunately the product, which was isolated in the form of almost colourless plates by crystallisation from either acetic acid or ethanol, proved to be accompanied by some tenacious impurity which defied removal by repeated sublimation under

reduced pressure and recrystallisation from the above solvents as well as petrol. As a result, a homogeneous compound with a satisfactory m.p. and analytical data was not obtained.

Nevertheless, the bulk of this material has been identified as one of the two possible tetrahydro-indeno[2,1-a]perinaphthenes,



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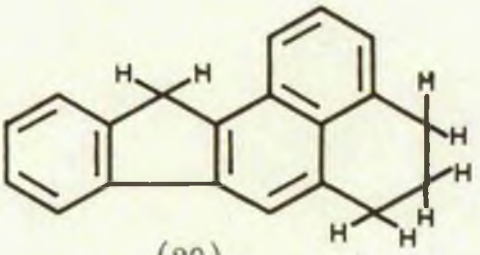

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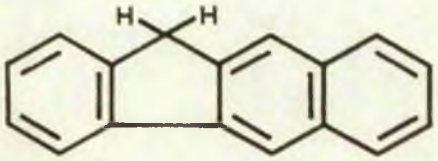

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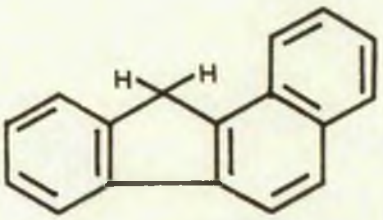

(31)

(28) and (29), or possibly a mixture thereof. Thus comparison of the absorption spectrum of the above product with those of authentic samples of 2:3-benzofluorene (30) (plate VI) and 1:2-benzofluorene (31) (plate VII) respectively has revealed correspondance in the positions and intensities of the band groups and maxima of the former and the latter two, tetrahydro-indeno[2,1-a]perinaphthene showing the expected bathochromic shift associated with poly-alkylation. The close similarity between the spectra of (30)and (31) did not permit of a decision being taken regarding the two possible structures (28) and (29) on this basis. In addition, in spite of the poor analytical data recorded for this hydrocarbon, the sym-trinitrobenzene and 2:4:7-trinitrofluorenone complexes have been prepared in an analytically pure condition.

Catalytic reduction of indeno[2,1-a]perinaphthene itself under identical conditions using Adam's platinum oxide catalyst yielded a colourless oil which did not crystallise. An attempt to identify this material gave indefinite results.

Summarising, it has been established that indeno[2,1-a]perinaphthene undergoes reduction at metal surfaces to yield a dihydro-derivative. The assignment of a structure to this hydrocarbon involving accession of hydrogen to position 12 on the one hand, and to either position 1, 3, 4 or 6 on the other is based both on a consideration of the fundamental properties of the system, and on the nature of the product afforded by further reduction. In conformity with the above, and with the observation that acid-catalysed isomerisation in the methylperinaphthene series results in a hydrocarbon in which the alkyl group is attached to a ring remote from that possessing the methylene group (A,IV,7), reduction in acid media is not regarded as affecting position 7. It is noteworthy that osmium tetroxide effects the dehydrogenation of the dihydro- derivative, as opposed to promoting the normal hydroxylation process.

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B,II,3. Evidence for the Identity of Di(indeno[2,1-a]perinaphthenyl).

It is pertinent at this juncture to review the evidence which has accumulated concerning the nature of the non-basic component of the mixture resulting from the acid cyclodehydration of the oxymethylene derivative (8).

It has been demonstrated that under the action of lead tetra-acetate, indeno[2,1-a]perinaphthene is converted to this hydrocarbon, and that this reaction is only satisfactorily accounted for by some form of intermolecular dehydrogenation. Furthermore, on prolonged treatment of the latter material with lead tetra-acetate, a compound

is obtained whose stoichometry corresponds to mono-acetoxy-di(indeno[2,1-a]perinaphthenyl).

The visible absorption spectra of indeno[2,1-a]perinaphthene and the non-basic hydrocarbon show considerable correspondance (plate IV), ε for the latter being approximately double that of the former. M. W. determinations have not proved conclusive, but the best value obtainable, 380, shows a considerable increase on that determined for (3).

There is therefore considerable support for the portrayal of this hydrocarbon as di(indeno[2,1-a]perinaphthenyl). Low basicity is attributed to linking across the 12:12' positions (10) of the indeno[2,1-a]-perinaphthene moieties, sites with which the basic properties of the latter are associated. In conformity with the latter, failure to enter into diene addition with maleic anhydride was observed.

The likelihood that this hydrocarbon is the alternative cyclisation product, benzo[a]naphtho[1,2-e]pentalene (11), rendered extremely improbable by reference to the properties of the closely related 1:2-4:5-dibenzopentalene (181; A,III,5), is now completely excluded by the preceding evidence.

The circumstances surrounding the formation of (10) are unusual, and no satisfactory mechanism can at present be advanced to account for it.

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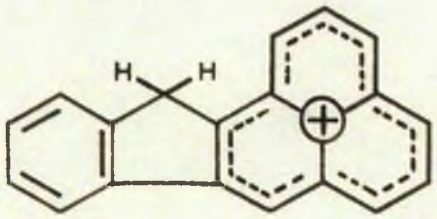
B.III. ELECTROPHILIC SUBSTITUTION OF INDENO[2,1-a]PERINAPHTHENE.

B.III.1. Basicity of Indeno[2,1-a]perinaphthene.



(9)

As was indicated in the account of azulene chemistry, the most characteristic property was ease of electrophilic substitution concomitant with high basicity, an identical fundamental process being assumed in each case. It is appropriate to preface a consideration of the former with some data on the latter property, which is more susceptible to quantitative measurement, and which may be regarded as a very pure form of electrophilic substitution.

As a similar situation is presumed to obtain in indeno[2,1-a]-perinaphthene as in azulene, the former would be expected to manifest basicity by analogy. On account of the postulated facile polarisability of (3) to yield a reacting form of type (15), accession of a proton should occur at position 12. The resulting conjugate acid (9) will be invested with considerable stability, being in effect a substituted perinaphthenylium cation. A quantitative measure of the basicity of this hydrocarbon is described below.

The addition of a proton to a neutral base may be represented by the equation,

$$B + H^+ = BH^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

The acidity constant, pK_{BH^+} of the acid BH^+ is defined by the equation

$$pK_{BH^+} = (a_{H^+}.a_B/a_{BH^+}.) \quad \ldots\ldots\ldots\ldots \quad (2)$$

where 'a' refers to the activities of the various species involved. It is possible to define an acidity function which expresses the tendency of a solution to protonate a neutral base in a similar fashion as the acidity constant in equation (2) is related to the reverse process. This function, commonly known as the Hammett function, is defined by

$$H_o = pK_{BH^+} - \log(a_{H^+} \cdot f_B / f_{BH^+}) \quad \ldots\ldots\ldots (3)$$

where 'f' represents the activity coefficients of the species involved. Experimentally it may be shown that normally (f_B/f_{BH^+}) approaches unity, and consequently the value of H_o is dependent only on the hydrogen ion concentration, and is a characteristic property of the acid solution. Combination of equations (2) and (3) gives as a result

$$H_o = pK_{BH^+} - \log(C_{BH^+}/C_B) \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where C represents the concentration of the appropriate species[21].

In order to adapt the above to the present context an additional quantity

$$P = (C_B/C'_B) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

must be introduced to formally express the distribution of the hydrocarbon base B between two immiscible solvents. C'_B and C'_{BH^+} represent the concentration of free base and the corresponding conjugate acid in the non-acidic phase (cyclohexane, toluene etc.). P. thus expresses the ratio of the solubilities of the base in both the acidic and non-acidic solvents. In practice it is observed that C'_B is very much greater than C'_{BH^+} and conversely C_{BH^+} is very much greater than C_B. Combining equations (4) and (5) results in

$$H_o = pK_{BH^+} + \log P + \log(C'_B/C_{BH^+}) \ldots (6)$$

Determination of (C'_B/C_{BH^+}) coupled with a previous knowledge of H_o leads to the evaluation of $(pK_{BH^+} + \log P)$. Unless a value can be assigned to P, which is virtually impossible in the case of hydrocarbon

bases, the fundamental quantity pK_{BH^+} which would serve to characterise the latter, remains indeterminate.

A compromise is possible whereby the so-called apparent partition coefficient $K' = (C'_B / C_{BH^+})$ is determined for a particular hydrocarbon for a series of acid concentrations, and the value of Ho for $(K' = 1)$ obtained by some suitable graphical method. From equation (6) it follows that in these circumstances

$$H_o = (pK_{BH^+} + \log P) \qquad (7)$$

and this could be regarded as a measure of the relative basicity of the hydrocarbon involved. Though treatment of the data is not rigorous, the determination of this Ho value has been of service in a comparative manner in connection with the azulene series[22].

Experimentally a known weight of hydrocarbon is distributed between a suitable organic solvent and acid solutions of previously determined strengths. When the system has come to equilibrium, the concentration of hydrocarbon in the organic phase is determined spectrophotometrically, and the concentration of the corresponding conjugate acid in the acid phase is calculated by difference. It has been found in practice with regard to the azulene series that Ho is dependent on $(pK_{BH^+} + \log P)$, and the latter appears to be a linear function of the former with a slope of about unity, or alternatively a plot of log K' against Ho is linear with a slope of about -2. This has been interpreted as due to a linear decrease in the logarithm of the solubility of base molecules in the acid with increasing values of Ho, or in practical terms an increase in solubility with increasing acidity[25]. This salting-in effect has been observed for the basic forms of oxygen compounds, and appears to be a fairly general one.

Indeno[2,1-a]perinaphthene was partitioned between cyclohexane and sulphuric acid of different strengths, and the resultant distribution between the two phases measured spectrophotometrically. A plot of Ho

against log K', utilising the data thus obtained, revealed that the value of H_0 for K' equal to unity (i.e., log K' = 0) was -4.80, the latter corresponding to an acid concentration of 64% (w/w)(plate IX). The slope of the straight line approximated to -2, in conformity with the previous observations. The values of H_0 for the concentrations of sulphuric acid used experimentally were obtained utilising a graph constructed from published data[34].

The corresponding values for a number of azulenes are recorded in table I for comparison. Perusal of the latter indicates that indeno[2,1-a]perinaphthene has a basicity which is fairly close to that of 5:6-benzazulene. Values determined for two different organic solvents vary significantly, and for two different acids vary considerably. With regard to the former, it would appear preferable to use organic solvents which have little likelihood of interacting with the acid phase, such as cyclohexane or petrol, but toluene has also been widely used.

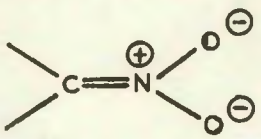
Azulene.	Organic Phase.	H_0	Acid. (% w/w)	Reference.
Azulene	Petrol	-3.00	47.8	(22)
	Toluene	-3.35	51.0	(22)
1-Methylazulene	Petrol	-2.96	47.3	(22)
	Toluene	-3.18	49.5	(22)
2-Methylazulene	Petrol	-2.54	43.0	(22)
	Toluene	-3.01	47.8	(22)
4-Methylazulene	Petrol	-2.69	44.7	(22)
	Toluene	-3.12	48.5	(22)
5-Methylazulene	Petrol	-2.30	40.3	(22)
6-Methylazulene	Petrol	-2.66	44.3	(22)
	Toluene	-3.27	50.4	(22)
2-Ethylazulene	Petrol	-2.73	45.1	(22)
2-Isopropylazulene	Petrol	-3.07	58.4	(22)
	Toluene	-3.07	50.0	(22)
2-(n-propyl)azulene	Petrol	-3.14	49.1	(22)
Guaiazulene	Petrol	-2.46	42.1	(22)
	Toluene	-2.53	42.9	(22)
Chamazulene	Petrol	-2.16	38.4	(22)
1:8-Trimethylene-azulene	Toluene	-3.56	52.9	(23)
4:5-Trimethylene-azulene	Toluene	-2.59	43.9	(23)
5:6-Trimethylene-azulene	Toluene	-3.32	50.7	(23)
1:2-Benzazulene	Toluene	-3.62	53.6	(23)
5:6-Benzazulene	Toluene	-4.51	61.7	(23)
cycloHepta[bc]-acenaphthylene	cycloHexane	-2.64	44.2	(19)

Table I. Basicities of Azulenes in Sulphuric Acid.

B,III,2. Electrophilic Substitution of Indeno[2,1-a]perinaphthene.

As a consequence of the observed basicity of indeno[2,1-a]perinaphthene, considerable susceptibility to electrophilic attack is to be expected. It was indicated above that, as a result of a consideration of the fundamental properties of the system, the conjugate acid (9) should be formed by accession of a proton to position 12. Analagous reasoning is applicable in the present context, and accordingly electrophilic substitution might be expected to manifest itself at the same position. This proposal has been in part confirmed experimentally.

Treatment of indeno[2,1-a]perinaphthene with tetranitromethane in absolute ethanol afforded a mononitro- derivative in the form of



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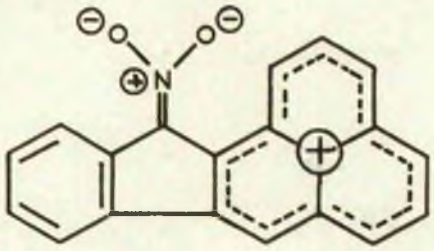

(33)

violet black prisms. The infra-red absorption spectrum of this compound, observed as a 'Nujol' mull, has indicated that the nitro-group bands occur at 1506cm.$^{-1}$ and 1307cm.$^{-1}$. The average value of the wavelength of the aromatic nitro- group band is 1520cm.$^{-1}$, and it has been suggested that increases in this wavelength are due to a larger contribution of the form (32)[26]. In the present case, this observation is entirely in conformity with proposed substitution at position 12, in which form (32) would be stabilised by conjugation with the perinaphthenylium cation, as in (33).

Indeno[2,1-a]perinaphthene has been shown to couple with diazotised p-nitro-aniline, but not with benzene diazonium chloride.

In order to test the conclusions arrived at regarding the position of electrophilic substitution, experiments were commenced involving the halogenation of indeno[2,1-a]perinaphthene. An attempt was made to effect iodination using silver trifluoracetate and iodine, but the resultant iodo- compound proved to be too reactive to permit of ready isolation, and rapidly evolved iodine and hydrogen iodide to give an intractable mixture.

On passing bromine vapour in nitrogen through a solution of (3) in carbon tetrachloride, bromination took place smoothly with concomitant formation of hydrogen bromide. The solid product, which was isolated, analysed well for monobromeindeno[2,1-a]perinaphthene, and afforded a sym-trinitrobenzene complex which likewise gave a satisfactory analysis. The monobromo- derivative did not possess a sharp m.p., and was thus suspected to be inhomogeneous. Further indications of the latter were obtained by virtue of the following reaction sequence which was designed to locate the position of substitution.

The bromo- derivative was heated in boiling nitrobenzene solution with maleic anhydride, and it was observed that a significant quantity of hydrogen bromide was evolved. The resulting product, which melted over a small range, was shown by analysis to contain 5.8% of brominated dicarboxylic acid anhydride. The latter inhomogeneous compound was subjected to decarboxylation by pyrolysis with soda lime, but the resultant hydrocarbon again appeared to contain 5.7% of brominated derivative. Finally, the impure hydrocarbon was debrominated using Raney nickel alloy in alkaline solution, whence a bromine free product identical with indeno[1,2,3-cd]pyrene (17) was obtained.

The rationale of the above reaction sequence permits of the interpretation that the bulk of the bromine in bromo-indeno[2,1-a]-perinaphthene was situated at either positions 1 or 12. The occurence of bromine in the anhydride obtained by Diels Alder addition could be accounted for if bromination were taking place at two sites silultaneously,

though predominately at one. The fact that the bromo- derivative itself appeared inhomogeneous tends to support this notion.

During the course of dienophile addition, hydrogen bromide is continuously evolved in an oxidising medium, and under the circumstances formation of free bromine followed by bromination of the adduct cannot be discounted. It is of particular interest that interaction of bromomaleic anhydride and 1:12-benzoperylene gave a coronene dicarboxylic acid containing 3.5% of bromine[3]. In the latter case, which bears considerable resemblance to the present context, unless some mechanism is derived whereby bromine contained in the primary adduct, which cannot be isolated, migrates on dehydrogenation, bromination after the formation of the fully aromatised adduct must be assumed.

In order to render the position regarding bromoindeno[2,1-a]-perinaphthene in a more satisfactory state, an attempt was made to rigorously purify the crude product in the form of the sym-trinitro-benzene complex by fractional crystallisation from ethanol, so that a homogeneous product would be available for the above reaction sequence. The impurity proved to be extremely tenuous, and after several crystallisations the m.p. was little improved, and the product obtained by maleic anhydride addition contained almost the same quantity of bromine as was found previously.

In view of the temperature at which the Diels Alder addition reaction is conducted, the question arises as to whether the primary process involved is not the formation of bromine and substituted perinaphthenyl radicals, followed by addition of dienophile at some site remote from the original source of the bromine. To investigate this possibility, bromoindeno[2,1-a]perinaphthene was treated in an identical fashion to that employed in the dienophile addition reaction, but in the absence of maleic anhydride. The coloured material in the resulting solution was found to be completely extractable into 86% sulphuric acid, which is sufficiently strong to dissolve the bromo-

derivative, but not products formed by dimerisation of the radical.

Finally bromoindeno[2,1-a]perinaphthene was subjected to oxidation under the action of chromic anhydride in acetic acid. The resultant quinone was found to contain 1.67% of bromine, corresponding to 7.6% of brominated quinone. It is of particular interest that infra-red absorption spectral measurements have indicated the presence of one oxygen atom as position 12 and the other in the perinaphthene moiety.

Summarising, it has been shown that indeno[2,1-a]perinaphthene may be placed alongside 5:6-benzanulene in order of basicity. The former hydrocarbon has been shown to be susceptible to electrophilic attack, and nitration and bromination have been demonstrated. Finally conclusive evidence has been presented that bromination takes place principally at positions 1 and 12, considerations related to fundamental theory favouring the latter position. A complication which arose in the orientation work has been discussed. Quinone formation and dienophile addition have been shown to involve at least one position in common.

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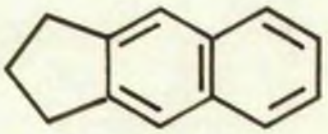
B,IV. cyclopenta[a]perinaphthene.

B,IV,1. cyclopenta[a]perinaphthene: Attempted Synthesis.



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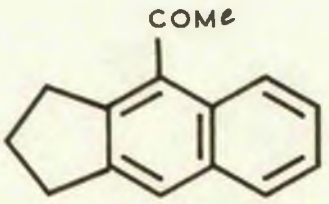

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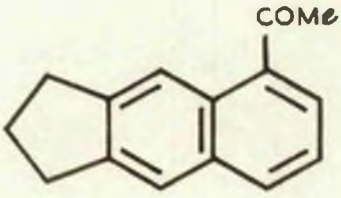

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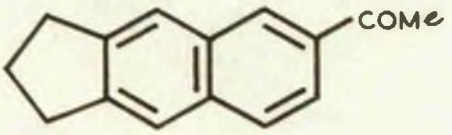


(37)

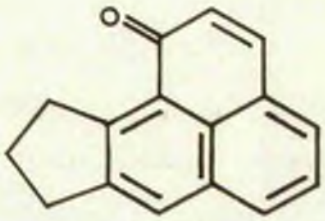
The hypotheses which were made in connection with cyclopenta[a]-perinaphthene (A,III,8) would appear to have found ample justification from a study of indeno[2,1-a]perinaphthene. The logical complement to the above investigation involves the synthesis of the former, fundamentally more important hydrocarbon. Accordingly experiments were initiated with this goal in view.

At the outset it was apparent that a strictly analogous reaction sequence to that employed in the synthesis of (3), involving as it does cyclodehydration of an oxymethylene derivative as the ultimate step, was not applicable in the present context. As an alternative, it seemed appropriate to proceed along a course which would yield a suitable perinaphthene, and to terminate the synthesis by dehydrogenation. Though perinaphthene had never been isolated from a dehydrogenation reaction, in view of the stability which is associated with the cyclopenta[a]perinaphthene system, there was good reason to believe

that the latter might survive the conditions obtaining in the ultimate step. The synthesis scheme eventually decided upon bears a close resemblance to that utilised in the first successful synthesis of perinaphthene itself (A,IV,3). The preliminary problem, therefore, entailed the preparation of a suitably acetylated hydrocarbon.

2:3-cyclopentenonaphthalene (34), acetyl chloride and aluminium chloride were permitted to interact in 1:2-dichlorethane solution. Such a Friedel-Crafts condensation could result in the production of any or all of the three isomeric mono-acetyl derivatives, (35), (36) and (37). In point of fact, the resultant product consisted largely of an oil and a small quantity of solid material, which was removed. The oil was subjected to a formylation procedure utilising ethyl formate in the presence of anhydrous potassium methoxide in ether. The corresponding oxymethylene ketone was obtained as a yellow oil which did not crystallise, and which was used immediately in the next step without further purification.

The oxymethylene derivative was cyclodehydrated by the gradual addition of 87% sulphuric acid to its solution in carbon tetrachloride at room temperature during the course of 10 minutes (cf. B,I,1). In practice considerable difficulty attended the isolation of an homogeneous perinaphthenone from this reaction. Thus the crude product, obtained by extraction of the reaction mixture with concentrated hydrochloric acid, was a brown oil which did not crystallise spontaneously, nor did it crystallise readily from its solution in petrol. It proved extremely prone to precipitation from saturated solutions as an unstable brown oil on the sides of the glass vessels used, and only by controlled cooling of such solutions was it possible to obtain crystalline material, which in contrast to the oil was quite stable. The latter, in the form of yellow needles, did not possess a sharp melting point, and was considered to be a mixture of the perinaphthenones (38) and (39).



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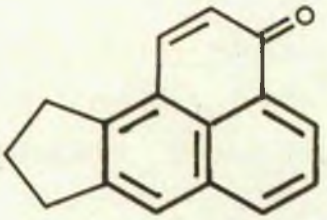


(39)

It will be apparent that of the three acetyl derivatives, (35), (36) and (37), only two can lead subsequently to perinaphthenones. The resultant oil from the acetylation reaction is accordingly a mixture of the former two corresponding to the mixture of perinaphthenones (38) and (39) obtained on cyclodehydration.

The difficulty surrounding the crystallisation procedure prompted an attempt to effect purification of the crude mixture of the perinaphthenones by an alternative process. Distillation under reduced pressure resulted in considerable loss of material, but the product crystallised readily from methanol (together with one mole of solvent of crystallisation) and subsequently from petrol, did not melt over a range, and showed no tendency to be deposited as an unstable oil. It was concluded that one of the isomeric perinaphthenones was thermolabile and had suffered complete destruction on distillation. The homogeneous material obtained after removal of the unstable isomer was utilised in the next step of the reaction sequence.

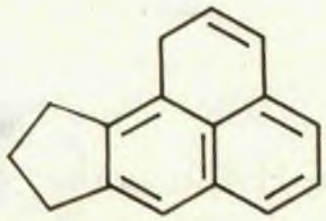
Though the oxymethylene ketone derived from (36) could conceivably undergo two different modes of cyclisation, and by way of the alternative mode involving position 7 of the naphthalene nucleus yield a benzindenone, recognition that the product of cyclodehydration is in fact a perinaphthenone is based on two facts. Thus the resulting ketone was soluble in concentrated hydrochloric acid, and this manifestation was made use of in its extraction from the crude reaction mixture. Furthermore, infra-red absorption spectral measurements on this compound

as a 'Nujol' mull in the solid state have indicated that the carbonyl stretching frequency band lies at 1637cm.$^{-1}$ and 1620cm.$^{-1}$ These values correspond well to those observed in other examples of perinaphthenones (A,IV,5; table II).

The solid product, in the form of colourless plates, which resulted from the Friedel-Crafts condensation was subjected to formylation procedure. The resultant oxymethylene ketone did not yield any useful material on cyclodehydration under the action of 87% sulphuric acid, from which it was deduced that the former ketone had structure (37). Thus acylation of (34) appears to result in the production of all the possible isomers, though presumably only one predominates.

The anomalous products obtained by reduction of perinaphthenones using such reagents as aluminium iso-propoxide and lithium aluminium hydride have already been the subject of comment (A,IV,4). The example in the present context did not prove exceptional and on reduction with the latter reagent gave a substituted perinaphthene,(40) representing one of a number of possible structures for the latter. The above hydrocarbon was obtained in good yield, in contrast to the yield of perinaphthene resulting from a similar reduction of perinaphthenone itself.

In the initial investigation of the reduction step, the metal-organic complex which is formed by the addition of lithium aluminium hydride to the ketone was decomposed in acid media, and a homogeneous product was obtained by crystallisation from petrol in the form of colourless prisms. In order to examine the possibility that acid-catalysed isomerisation was occurring, the decomposition step was conducted using aqueous ammonium chloride solution. The resultant hydrocarbon was a mixture, and separation of the components by fractional crystallisation proved to be too protracted for the quantity of material available, though the melting range suggested that one of the components was identical with the homogeneous perinaphthene obtained previously.



(40)

The attempted aromatisation of the above homogeneous cyclopentenoperinaphthene was unfortunately without successful outcome. Thus on dehydrogenation by standard procedures involving palladised charcoal at 270–300°, and sulphur at 180–210°, an intractable high melting tar was obtained in each case. When a solution of the hydrocarbon in carbon tetrachloride was boiled under reflux in the presence of N-bromsuccinimide no useful product could be isolated. With regard to the latter, it has subsequently been revealed that under these conditions radical formation with subsequent polymerisation is likely to be the preferred mode of reaction. The quantity of material available did not permit of a more detailed investigation using refined techniques, but it would appear that thermal instability of the product militates against its survival under the vigorous conditions obtaining during dehydrogenation.

In conclusion, though the above synthesis was attended with failure in the final step, it must be regarded as premature to deduce that cyclopenta[a]perinaphthene is incapable of a stable existence or of displaying suitable properties. Doubtless the highly developed aromatic character displayed by indeno[2,1-a]perinaphthene is in part due to annelation of benzene on to the five-membered ring, and conclusions derived from a study thereof can only be applied with some reservation to the parent system. It is suggested that provided a terminating step to the reaction sequence is devised which employs mild conditions, this synthesis may yet prove successful.

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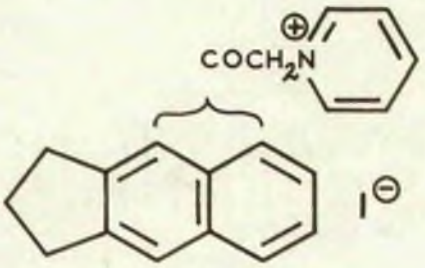
B,IV,2. cycloPenta[a]perinaphthene: Synthetic Approach to the Isomeric 2:3-cycloPentenonaphthalene Carboxylic Acids.

Though the preparation of cyclopenta[a]perinaphthene had been unsuccessful, it seemed pertinent to resolve the problem of the identity of the products obtainable by Friedel-Crafts acylation of 2:3-cyclopentenonaphthalene (34), and if possible to elucidate the structure of the homogeneous cyclopentenoperinaphthenone. At the outset, it was considered appropriate to degrade the known acetyl derivatives to the corresponding carboxylic acids, which should be suitably crystalline compounds for characterisation, and for comparison with a carboxylic acid of known structure synthesised by unequivocal procedure. Though the former object was achieved with little difficulty, a complication arose in the latter which rendered the preparation of the key compound in this structural investigation impossible.



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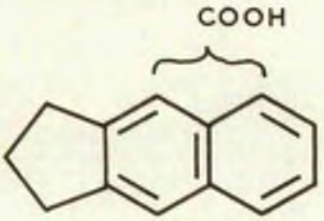
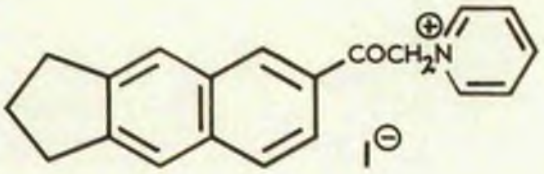


(42)

Treatment of the oil resulting from the acylation of (34) with iodine in boiling pyridine afforded the pyridinium iodide (41). The latter salt was hydrolytically cleaved by the action of aqueous: alcoholic potassium hydroxide, and an homogeneous crystalline carboxylic acid obtained. This acid, produced in somewhat low yield, must possess the formula either of 2:3-cyclopentenonaphthalene-1-(or -8-)carboxylic acid (42), corresponding to whichever of the respective ketones (35) or (36) predominate in the original mixture. The above degradation is a modification[27] of the well-known method developed by Krönke[28].



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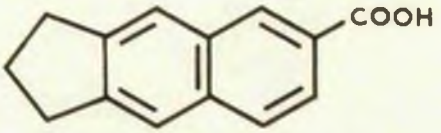
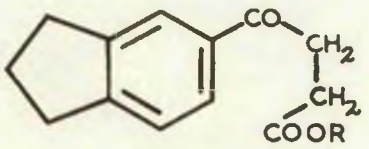


(44)

The solid component of the mixture resulting from the acetylation of (34) was treated in an identical manner, and an homogeneous, crystalline carboxylic acid obtained in good yield. This acid and the corresponding pyridinium iodide, which differed from (42) and (41), were formulated as (44) and (43) respectively on the basis of the structure assigned to the ketone (37) in (B,IV,1).

At this juncture it became necessary to prepare a 2:3-cyclopentenonaphthalene-1-(or -8-)carboxylic acid of known structure for comparison with (42), so that the exact formula of the latter would be determined. The following reaction scheme was adopted as representing the most reasonable approach to the synthesis of such an acid whose structure would be indicated unequivocally.



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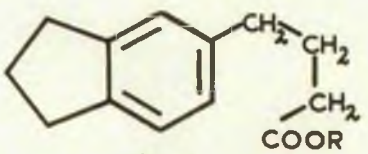

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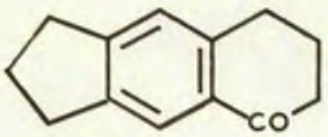

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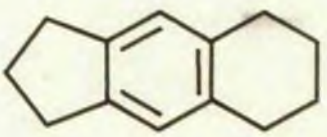
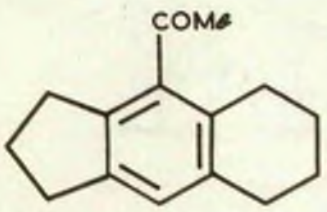


(48)

Indan undergoes succinoylation in nitrobenzene solution at room temperature under the action of succinic anhydride:aluminium chloride complex to yield γ-keto-γ-indanylbutyric acid (45; R = H)(C,VII,1 et seq.). Reduction of the ester (45; R = C_2H_5) by Clemmensen procedure affords γ-indanylbutyric ester (46; R = C_2H_5). Cyclodehydration of the acid (46; R = H) using 85% sulphuric acid gives the ketone (47), which may be reduced by hydrogen in the presence of Adam's platinum catalyst to yield 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (48).

The hydrocarbon (48) was subjected to acetylation by the action of acetyl chloride:aluminium chloride complex in 1:2-dichlorethane solution at room temperature. The product proved to consist of a colourless oil and a small quantity of colourless, crystalline solid, which was removed. It will be appreciated that provided the above Friedel-Crafts condensation is not beset with complications, only one mono-acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (49) is



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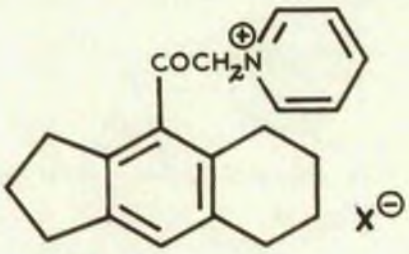

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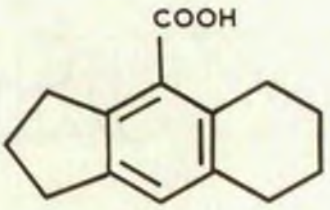


(51)

possible. However both solid and liquid components of the reaction product analysed well for (49), and the significance of this fact and the results of further investigations are considered in detail later.

In order to accomplish the conversion to the expected carboxylic acid (51), hypohalite oxidation of the latter ketone was attempted. On treatment of the liquid fraction corresponding to mono-acetylated 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene with sodium hypochlorite a colourless, crystalline carboxylic acid was obtained in low yield which melted over a considerable range, and was considered inhomogeneous.

To obviate any complications inherent in the latter process, degradation was effected by first forming the pyridinium salt (50; X = I) followed by hydrolytic cleavage according to the method described previously. By this means a very small quantity of a homogeneous, colourless carboxylic acid was prepared.

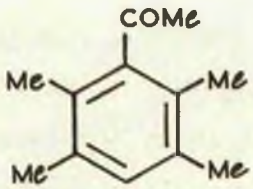
In order to obtain the desired product, two moles of hydrogen require to be abstracted from (51). Accordingly the above acid was converted to its methyl ester through the agency of diazomethane, and then subjected to the action of 20% palladised charcoal at 250-300°, during the course of which hydrogen was freely evolved. A crystalline, carboxylic acid was isolated in good yield which, however, proved to be a mixture and was accordingly given further treatment with the palladised charcoal catalyst at a slightly elevated temperature than used previously in order to dispose of the possibility that dehydrogenation had been incomplete. The resulting product displayed little improvement.

In order to facilitate the production of the pyridinium salt, and at the same time dispense with the wasteful iodination step so as to render more carboxylic acid available for investigation, acetyl chloride was replaced by chloracetyl chloride in the Friedel-Crafts condensation which was conducted in an otherwise identical fashion. The expected 1-chloracetyl-2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene proved to have suffered hydrolysis in the working-up process, for on interaction with pyridine only a small quantity of the corresponding pyridinium salt (50; X = Cl) was deposited. Hydrolytic cleavage of the latter resulted in a colourless, crystalline carboxylic acid which melted over a considerable range, and was subsequently treated with sulphur at 150-300° during the course of which hydrogen sulphide was freely evolved. The resultant acid possessed no more satisfactory properties than that obtained in the former dehydrogenation reaction. The outcome of this particular experiment removes the possibility that partial dehydrogenation was occurring at some stage other than the terminal one, and that

rearrangement was accompanying catalytic dehydrogenation.

The complication which has frustrated all the attempts to prepare an homogeneous 2:3-cyclopentenonaphthalene carboxylic acid of known structure appears to have its origin in the acylation step. Such a complication could arise either immediately before or after condensation of the acyl halide:aluminium halide complex with the hydrocarbon, the outcome in either case being different. Thus the hydrocarbon (48), corresponding to durene in susceptibility towards the influence of Friedel-Crafts-type catalysts, might be expected to provide a suitable vehicle for isomerisation reactions through the agency of aluminium chloride. The effectiveness of aluminium halides in this direction is considerably attenuated when the latter is combined with an acyl halide. During the execution of all the Friedel-Crafts condensations great attention was paid to ensuring that all the metal halide catalyst was brought into contact with the hydrocarbon (48) in the form of the corresponding acyl halide complex only by using a slight excess of the latter. Accordingly it seems reasonable on this basis to discount the possibility that isomerisation was preceding acylation.

On the other hand, the isomerisation of o-alkylaryl ketones in the presence of aluminium halide and hydrogen halide has been thoroughly investigated and the data rationalised [29][30][31]. The most relevent example in connection with the present context involves the irreversible transformations of acetyldurene (52) to 2:3:4:5-tetramethylacetophenone (53), and of 9-acetyl-sym-octahydro-anthracene (54) or 9-acetyl-sym-octahydrophenanthrene (55) to 7-acetyl-2-methyl-4:5-cyclohexeno-indan (56). These isomerisations, which were all effected in high yield, were conducted in a melt of sodium and aluminium chloride at 100°[31].



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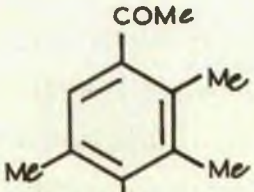

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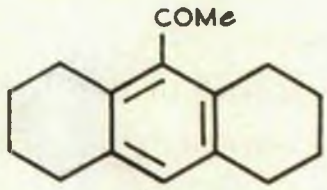

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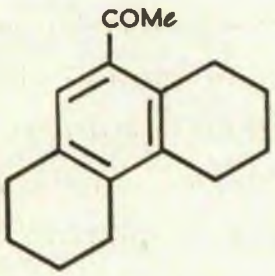

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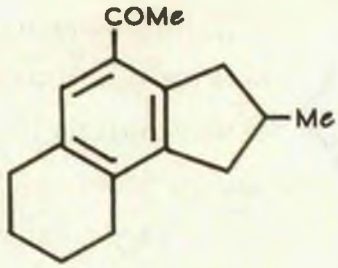

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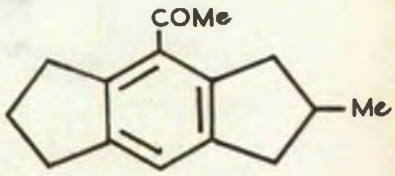


(57)

The formal analogy between the present case and the examples cited above is obvious, though this does not extend to the physical conditions employed. It is not illogical to suppose that an isomerisation which proceeds to completion under forcing conditions might well occur to a significant extent under milder conditions and give rise to a mixture which could not be effectively separated into its components. Applying this reasoning to the present context, 1-acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene which is initially formed may be considered to undergo partial isomerisation under the action of hydrogen chloride:aluminium chloride to give (57). Such a transformation has as its driving force the lessening of steric interaction between the acyl and vicinyl alkyl groups which results from the ring contraction, and in addition is the only account of this reaction which permits of a satisfactory interpretation of all the observed phenomena. Thus the production of an inhomogeneous carboxylic acid by catalytic dehydrogenation of a homogeneous hydro-aromatic precursor, detailed previously,

could be explained if the latter were (57), and the former a mixture of (57) and a naphthalene carboxylic acid (42) resulting from ring expansion and subsequent loss of hydrogen.

In order to test the conclusion that the cause of the above isomerisation lay in the use of aluminium chloride, identical acylation experiments were conducted in which the latter was replaced by stannic chloride. In two successive preparations, the hydrocarbon (48) was condensed with acetyl chloride:stannic chloride complex at room temperature using alternately 1:2-dichlorethane and nitrobenzene as solvents. The latter modification was introduced in the hope that further protection would be afforded the resultant acetyl derivative by virtue of the attenuated influence of the catalyst by complex formation with the solvent. The products in each case were degraded by Krönke's method as detailed previously. The resultant, crystalline carboxylic acids which appeared to be identical, both melted over a considerable range which was little improved by recrystallisation, and attempts at further purification were abandoned. The isomerisation through the agency of stannic chloride implied by this result was somewhat unexpected, and is seldom demonstrable for the latter catalyst.

It has been recorded that anthracene-9-carboxylic acid may be obtained by the action of oxalyl chloride on anthracene in boiling nitrobenzene solution[32]. The reaction conditions employed here had obvious appeal in that a carboxylic (or glyoxylic) acid results directly, and complications associated with Friedel-Crafts-type catalysts are absent. On repetition of this experiment replacing anthracene by (48) only starting material could be isolated, which is somewhat remarkable in view of the somewhat greater reactivity expected of the latter hydrocarbon with respect to the former. When oxalyl chloride:aluminium chloride complex was condensed with (48) in nitrobenzene at room temperature, a small quantity of a homogeneous, pale yellow, crystalline carboxylic acid was isolated which did not correspond to any which had been prepared before. No explanation can be offered at present to

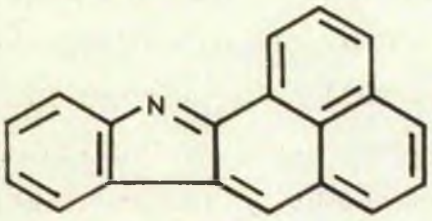
account for the latter.

The above work was carried out in ignorance of the fact that a preparation of (51) had already been described in the literature[33]. Persual of the relevent manuscript indicated that the reaction was executed in an almost identical fashion to that detailed in (C,VII,5), with the exception that acetic anhydride replaces acetyl chloride. Unfortunately these workers did not attempt to assess the purity of their product by characterisation through a suitable derivative, and the homogeneity or otherwise of the latter is therefore not established. An attempt to degrade (51) to the corresponding carboxylic acid was reported to have been unsuccessful (cf. C,VII,8). This work has not yet been repeated, and so it is premature to pass judgement on what importance may be attached to such a modification. However the absence of hydrogen halide derived from the acylating agent may be relevent in that presence of the former appears to be a prerequisite in many of the isomerisations conducted through the agency of aluminium chloride[31].

In conclusion the research work described in the above account must be regarded in the nature of a preliminary investigation, and further experiments are being conducted with a view to determining the optimum conditions required for Friedel-Crafts condensation involving (48). In this connection, the current results would seem to indicate that a combination of acetic anhydride and boron trifluoride offers the most hope of success. The author regrets that limitations imposed by the time available necessitated the termination of this study at an incomplete stage in order that it might be included in the present thesis.

++++++++++++++++++++++++++++++++

B.V. INDOLO[2,3-a]PERINAPHTHENE.



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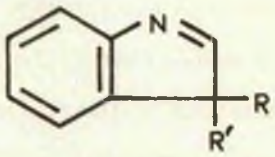

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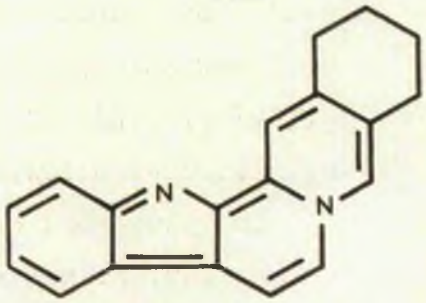
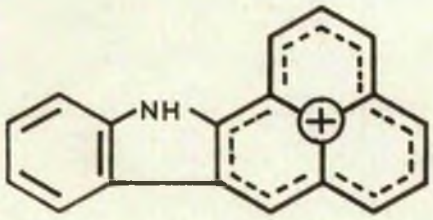


(60)

Some interest attaches to the attendant modifications of physical and chemical properties accompanying the replacement of carbon 12 in indeno[2,1-a]perinaphthene by nitrogen. The five-membered ring in this aza-analogue, indolo[2,3-a]perinaphthene (58) bears a resemblance to its counterpart in the indolenine series (59; R,R' = alkyl or aryl etc.,) as opposed to the indole series. A closer formal analogy may be drawn between the corresponding moieties in the present case and 1-aza-azulene on the one hand, and the carboline system in the alkaloid sempervirine (60) on the other.



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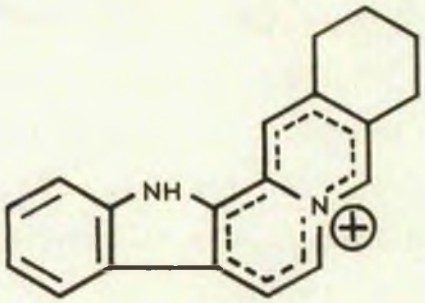
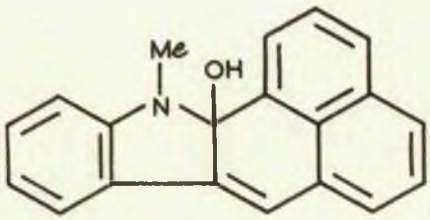


(62)

Simple indolenines (59) are basic in character and are rather unstable, being unable to revert to the more stable indole structure, which is by contrast acidic. When contiguous with the perinaphthene moiety, enhanced stability of the conjugate acid with a concomitant increase in basicity is to be expected as a result of the delocalisation energy invested in the perinaphthenylium cation with which the unit

positive charge will be partly associated. In a likewise manner the conjugate acid of (60) is stabilised by association of the positive charge with the pyridocoline moiety. Comparison of the basicity constants of (58) and (60) should therefore be a qualitative measure of the relative stabilities of the cations in (61) and (62).



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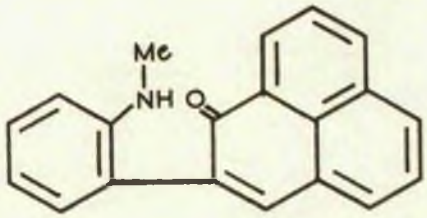
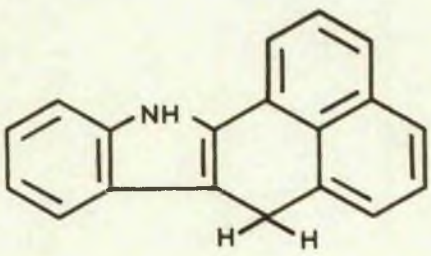


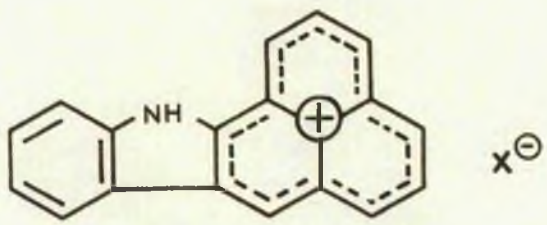
(64)

Furthermore the pseudo base derived from the methiodide of (58) merits examination. Accession of an hydroxyl group to the perinaphthene moiety (63) followed by spontaneous cleavage to give the perinaphthenone (64) is the postulated course of this reaction. Such ring scission would normally be reversible, but in view of the attenuated carbonyl reactivity associated with perinaphthenone (and tropone), facile recyclisation may well prove impossible.

Interaction of perinaphthan-1-one with phenylhydrazine in boiling ethanol gave perinaphthanone phenylhydrazone. Treatment of the latter in boiling acetic acid solution for a short period (1½ minutes) afforded the expected indole derivative (65). Alternatively the two processes could be conveniently combined as is the practice in the Fischer Indole synthesis to give (65) directly from perinaphthanone. This compound when obtained pure in the form of almost colourless plates is quite stable, but deteriorates rapidly in solution.



(65)



(66)

On treatment of (65) with iodine in boiling methanol, spontaneous dehydrogenation occurred with comitant formation of hydrogen iodide, and as a consequence only the salt (66; X = I), which crystallised in the form of black needles, was obtained. Analytical data indicated that the latter was contaminated with a small quantity of the corresponding periodide (66; X = I_3). Basification of this salt with either sodium carbonate or sodium hydroxide resulted in the production of an intensely red-coloured solution (in ether), but only a black friable solid could be recovered on removal of the solvent and this proved insoluble in both ether and benzene. In view of the latter, it was deduced that the free base (58) was insufficiently stable to permit of isolation.

As an alternative to the latter, the salt (66; X = I) was treated with an excess of 72% perchloric acid in methanolic solution to effect conversion to the perchlorate (66; X = ClO_4). This could also be conveniently prepared directly by boiling a solution of perinaphthanone phenylhydrazone in acetic acid containing 72% perchloric acid in an inert atmosphere. The salt was deposited from the reaction solution in an analytically pure condition, and recrystallisation from acetic acid was without marked improvement. From the conditions employed in the above reaction, it must be implied that (65) undergoes acid-catalysed dehydrogenation without the participation of oxygen, which is doubtless a reflexion on the delocalisation energy obtaining in the resultant system.

The visible and ultra-violet absorption spectra of indolo[2,3-a]-perinaphthene perchlorate (66; X = ClO_4) in methanol, and indeno[2,1-a]-perinaphthene and its corresponding conjugate acid are combined for comparison on plate VIII. The spectra of (66; X = ClO_4) and the latter hydrocarbon show considerable superficial correspondance. This is not entirely unexpected, for notwithstanding whatever influence the presence of a unit charge may have, the salient features of the mobile electron system obtaining in the free base (58), iso-electronic with (3), survive in the conjugate acid (61) through involvement of a pair of 2p electrons

from the hetero- atom. By contrast the delocalised electron framework of indeno[2,1-a]perinaphthene cannot be retained in the conjugate acid (31), and in conformity the visible absorption spectrum of the latter shows significant alteration.

This investigation is at present being continued.

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(For explanation of abbreviations used see 'Literature Cited, Part A.)

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(30) ibid., (1950), 994.

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(32) Latham, May and Mosettig, J.A.C.S., 70 (1948), 1079.

(33) Arnold and Rondesvedt, J.A.C.S., 68 (1946), 2176.

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PART C.

N O T E S.

Where original literature is cited, this is indicated by numbers in parentheses and superscript, a key to which will be found at the end of part C.

The ultra-violet and visible absorption spectra were measured on a 'Unicam' S.P. instrument.

The melting points were determined on a Kofler-type heating stage.

Micro-analyses were conducted by Drs. Weiler and Strauss, Oxford.

Unless otherwise stated, acid concentrations are expressed in terms of a percentage weight in weight (%w/w).

The terms light petrol and petrol refer respectively to those solvents more commonly designated as petroleum ether (b.p. 40-60°) and petroleum ether (b.p. 60-80°).

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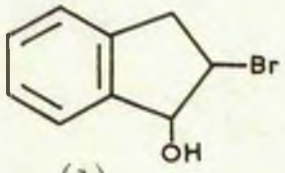
C.I. SYNTHESIS OF INDENO[2.1-a]PERINAPHTHENE.

C.I.1. 2-bromo-1-hydroxyindane[1].

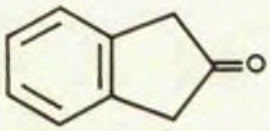


(1)

Bromine (70gm.; 23.0ml.) in aqueous potassium bromide solution (400ml.) was added to a vigorously stirred suspension of indene (50gm.) in water (1 litre) during the course of 15-30 minutes. The product (1), which crystallised on cooling, was filtered off, washed successively with water, light petrol, water and finally petrol, and was recrystallised from ethanol.

Yield: 365 gm., (62% from 320 gm. indene).
M.p.: 126-128° (Lit: 128-130°).

C.I.2. Indan-2-one[2][3].



(2)

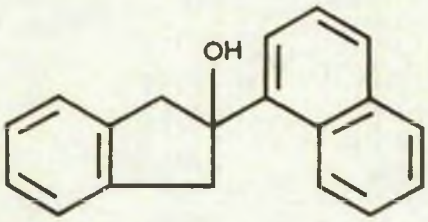
A solution of potassium hydroxide (84gm.) in water (600ml.) and alcohol (900ml.) together with 1-bromo-2-hydroxyindane (315gm.) was boiled under reflux for 60 minutes. After the bulk of the alcohol and some of the water had been removed by distillation, the solution was acidified by the addition of concentrated sulphuric acid (60ml.) in water (300ml.) and the whole boiled under reflux for 15 minutes, the 2-indanone (2) being subsequently obtained by steam distillation (2.5 - 3 hours; 3 litres distillate.) The crude solid was taken up in ether.

The solution was subsequently dried over anhydrous sodium sulphate. After removal of the ether on the water bath, the pure 2-indanone was obtained as colourless needles by trituration of the residual oil with light petrol. A small quantity of product was obtained by concentration of the mother liquors.

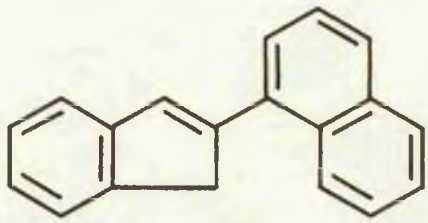
Yield:	100.5 gm.,(50%)	(92 gm. spont. plus 8.5 gm. ex mother liquors. Lit: ca. 75%).
M.p.:	58°	(Lit: 58°).

Note 1. It was observed that maintaining the original reaction mixture slightly acid improved the yield of product to ca. 65%.

C.I.3. 1-2'-Indenylnaphthalene.



(3)



(4)

A solution of indan-2-one (2) (100gm.) in ether (300ml.) was added to the well stirred Grignard reagent prepared from 2-bromonaphthalene (233gm., 155ml., i.e., 1.5 moles - 50% excess over 2-indanone) and magnesium (27.6gm.) in ether (1000ml.) during 45 minutes, the whole being cooled in an ice bath. At the conclusion of the addition, the reaction mixture was boiled under reflux for one hour during which time the ether was gradually replaced by benzene until the boiling point of the solution had reached 78°(ca. 1800ml. of solvent removed). Boiling under reflux was continued for a further 6 hours.

The cold reaction mixture was poured into an excess of 4N sulphuric acid cooled in an ice bath, and the benzene layer washed successively with water, and after removal of solvent by evaporation was then subjected to steam distillation to remove naphthalene (3 hours; ca. 6 litres distillate note 1).

The residue was taken up in benzene and after drying over sodium sulphate, the benzene was removed on the water bath and the residue distilled at reduced pressure. The fraction boiling at 170-210°/0.7 mm. consisting of a mixture of carbinol (3) and its dehydration product (4) was obtained as a light brown viscous oil (note 2).

The foregoing mixture was completely dehydrated by boiling under reflux in glacial acetic acid (300ml.) and 98% formic acid (250ml.) for 2 hours. The cooled solution was poured on to a mixture of crushed ice and water, and the product taken up in ether. The ether solution was washed successively with water, 20% sodium hydroxide solution (twice) water, and finally dried over anhydrous sodium sulphate. After removal of the ether on the water bath, the residual brown oil was taken up in benzene:petrol (1:8), and the solution filtered through a column of alumina (9 x 4.2 cm.). A strongly held zone of yellow impurity remained at the top of the column. On evaporation of the almost colourless eluates the hydrocarbon was deposited in its metastable form (note 3) as colourless needles which may be recrystallised from petrol.

Yield:	46.1 gm., (82%).	
M.p.:	77-79°, (metastable form)	
Analysis:	Found;	C, 94.0; H, 6.0%
	$C_{19}H_{14}$ requires;	C, 94.2; H, 5.8%

The sym-trinitrobenzene complex was prepared by heating together equimolecular proportions of the hydrocarbon and sym-trinitrobenzene in absolute ethanol. Recrystallisation from ethanol yielded the complex in the form of elongated prisms.

M.p.:	142-143°	
Analysis:	Found;	N, 12.4%
	$C_{19}H_{14}C_6H_3O_6N_3$ requires;	N, 12.4%

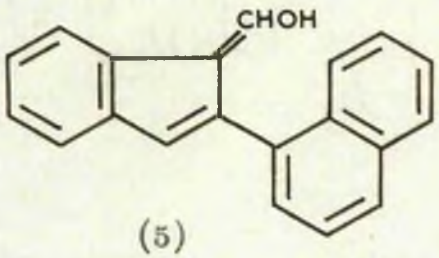
Note 1. The procedure may be modified at this stage in that the benzene extract may be dried over sodium sulphate and the benzene

removed at the water bath. The residual dark oil is then subjected directly to distillation under reduced pressure and the first fraction boiling at 95-140°/18 mm. consists mainly of naphthalene. The procedure then follows as detailed. The practical difficulties which attend the removal of naphthalene by such a method make its removal by preliminary steam distillation preferable.

Note 2. Elementary analysis of the product at this stage indicated that the carbinol (3) and its dehydration (4) product were present in the proportions of seven to one.

Note 3. The hydrocarbon was shown to exhibit dimorphism as the melt obtained by fusion of the metastable form resolidified to a mass of colourless plates at 81-84° which subsequently melted at 90-91°. The stable modification was obtained directly by subjecting the crude hydrocarbon to distillation and collecting the fraction at 184-187°/0.7 mm. This was taken up in benzene:petrol (1:8) and chromatographed on alumina. On evaporation of the eluates, the stable modification crystallised as colourless plates.

C.I.4. 1-(1-hydroxymethylene-2-indenyl)Naphthalene.



(5)

1-2'-Indenylnaphthalene (9.7gm.; 0.04 mole) was added to a suspension of dry alcohol-free potassium methoxide (3.2gm.;0.44 mole, i.e. 10% excess) in 75ml. of dry ether. Ethyl formate (3.3gm.; 0.044 mole, i.e. 10% excess), dried over potassium carbonate and subsequently distilled, was added to the above and the whole was boiled under reflux on the water bath for 3 hours, the solution becoming dark green in colour.

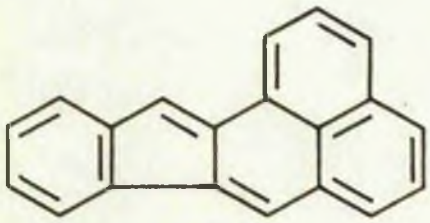
The potassium salt of the hydroxymethylene compound (5) was extracted into water from the cold solution at the end of the reaction, and the orange coloured product was taken in ether on acidification with dilute hydrochloric acid. The ether solution was washed once with water, once with saturated sodium bicarbonate solution and twice with water, and eventually dried over sodium sulphate. On removal of the other on the water bath, the product (5) was obtained as an orange coloured oil which did not crystallise but suffered decomposition on standing (Note 1), and very rapid decomposition on attempted distillation.

As a consequence of its tautomeric nature, 1-(1-hydroxymethylene-2-indenyl)naphthalene forms derivatives typical of aldehydes on the one hand and enols on the other. It was accordingly characterised by the preparation of its 2:4-dinitrophenylhydrazone(orange-red prisms from propionic acid), and of its benzoate obtained by the action of benzoyl chloride on the ethanolic solution of the compound in the presence of sodium ethoxide (yellow prisms from acetic acid).

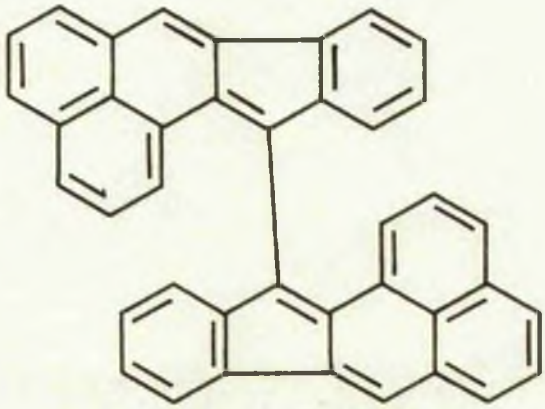
Yield:		8.75 gm.,(81%)	
M.p.:	(2:4-dinitrophenylhydrazone):	242-244°	
Analysis:		Found;	N, 11.9%
		$C_{26}H_{18}O_4N_4$ requires;	N, 12.4%
M.p.:	(benzoate)	175-177°	
Analysis:		Found;	C, 86.3;H,4.9%
		$C_{27}H_{18}O_2$ requires;	C, 86.6;H,4.8%

Note 1. Owing to the slow decomposition of the hydroxymethylene compound, it was found that the best yields of cyclised material (see below) were obtained when the working up procedure was carried out as rapidly as possible, and the crude oil cyclised immediately. Extension of the initial reaction time for periods of up to 6 hours did not materially affect the yield.

C.I.5. Indeno[2.1-a]perinaphthene.



(6)



(7)

1-(1-hydroxymethylene-2-indenyl)naphthalene prepared from 1-2'-indenylnaphthalene (9.7gm.) was dissolved in 200ml. of dry benzene (note 1). 93% Sulphuric acid (note 2)(200ml.) was added to the benzene solution previously heated to ca. 55° (note 3), and the whole was thoroughly shaken together during 45 seconds (note 4). The reaction mixture then was diluted with an excess of crushed ice and water, whence a reddish brown solid was precipitated. The brown solid was filtered off and washed free of benzene with ether, the washings being dark red in colour and containing a quantity of the product. The filtered residue was washed successively with water, sodium bicarbonate solution, and water and air dried.

The benzene:ether extracts in the filtrate were separated, washed once with water, twice with 20% sodium hydroxide, once with water, and dried over sodium sulphate. The solvent was largely removed by evaporation on the water bath, and the concentrated solution was added to the benzene extracts (below).

The air dried brown solid (above) was extracted in a soxhlet apparatus with boiling benzene until the extracts turned from deep red to brown in colour (ca. 1 hour). The extracts were shaken with water, 20% sodium hydroxide (twice), water and dried over anhydrous sodium sulphate.

The combined benzene solutions from the washings (above) and the extracts were taken down to low volume and chromatographed on alumina (9 x 2.4 cm.) to effect a preliminary purification. The column was eluted with benzene:petrol (1:4) and the crimson eluates concentrated to ca. 500ml.

Indeno[2,1-a]perinaphthene (6) was separated from an accompanying cyclisation product by a method utilising its greater basicity (note 5). The eluates from the preliminary chromatogram were extracted with four 200ml. portions of a cold mixture of 98% sulphuric acid and water (2:1), the acid extracts being initially deep green, but became paler. The hydrocarbon was recovered,by diluting the acid solution with an excess of crushed ice and water, as a reddish brown solid which was subsequently taken up in ether to give a blood-red solution. The ether solution was washed with water, 20% sodium hydroxide, water and dried over sodium sulphate. After removal of the ether on the water bath, the partly crystalline solid was taken up in benzene and the resulting solution was chromatographed on alumina (9 x 2.7 cm.) using benzene as developer and eluant. Evaporation of the eluates gave indeno[2,1-a]perinaphthene (6) as reddish brown leaflets.

Yield:	0.710 gm.,(7.8%).	
M.p.:	210-211° (sublimation)	
M.W.(Rast):	243.	
	$C_{20}H_{12}$ requires; 252.	
Analysis:	Found;	C, 95.1; H, 4.9%
	$C_{20}H_{12}$ requires;	C, 95.2; H, 4.8%

The sym-trinitrobenzene complex was prepared by boiling under reflux equimolecular quantities of the hydrocarbon (6) and sym-trinitrobenzene in ethanol, and subsequent recrystallisation from ethanol (black needles).

M.p.: 175–176°

Analysis: Found; N, 8.7%

$C_{20}H_{12}C_6H_3O_6N_3$ requires; N, 9.0%

The dark purple benzene solution remaining after acid extraction (above) was washed free of acid and dried over anhydrous potassium carbonate. The solution was concentrated on the water bath and chromatographed on alumina (9 x 2.7 cm.) using benzene:petrol (3:2) for development and elution, the elution being continued as long as the eluates possessed a dark purple colour. The eluates, on concentration to low volume, gave di(indeno[2,1-a]perinaphthen-12-yl) (7) in small violet-black prisms.

Yield: 0.210 gm., (2.08%)

M.p.: 294–297°

M.W.(Rast): 380

$C_{40}H_{22}$ requires; 503.

Analysis: Found; C, 95.0; H, 4.8%

$C_{40}H_{22}$ requires; C, 95.6; H, 4.4%

Note 1. Though it was found possible to cyclise the hydrocarbon using very much less benzene, i.e., 20ml. the yields were not consistent and a larger proportion of di(indeno[2,1-a]perinaphthen-12-yl) was produced.

Note 2. The concentration is critical, and practically no useful material at all is produced using concentrations of less than 89% or greater than 95%. The cyclising acid is readily prepared by mixing 100ml. of 98% sulphuric acid with 10ml. water.

Note 3. A slight improvement in yield of product was observed using the preheated benzene solution, but the temperature is by no means critical and reasonable yields are obtained from solutions at room temperature.

Note 4. Though 45 seconds appears to be the optimum time, this can be increased to 90 seconds without appreciable change in yield. Beyond

120 seconds, however, the yield drops off sharply.

Note 5. This represents a convenient acid concentration i.e., 77% though the hydrocarbon dissolves in 64% and lower.

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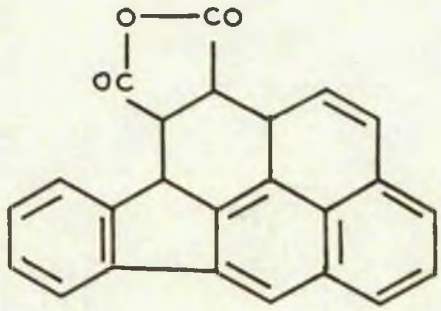
C.II. DIENOPHILE ADDITION TO INDENO[2,1-a]PERINAPHTHENE: FIRST SYNTHESIS OF INDENO[1,2,3-cd]PYRENE.

C.II.1. 10b:11:12:12a-Tetrahydroindeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride.



(8)

Maleic anhydride (30mgm.) in glacial acetic acid (7ml.) was added to a boiling solution of indeno[2,1-a]perinaphthene (50mgm.) in xylene (3ml.) and glacial acetic acid (8ml.) and the whole boiled under reflux for 5 minutes. On cooling the reaction solution 10b:11:12:12a-tetrahydro-indeno[1,2,3-cd]pyrene (8) crystallised out as colourless needles in almost quantitative yield.

Yield:

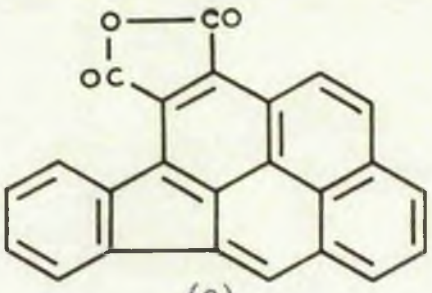
M.p.: ca. 260° (note 1).

Analysis: Found; C, 82.8; H, 4.1%

$C_{24}H_{14}O_3$ requires; C, 82.2; H, 4.0%

Note 1. This m.p. was determined on a preheated block. If an attempt is made to determine the m.p. by slow heating, the adduct does not melt sharply but becomes progressively darker from 230° to ca. 400°.

C.II.2. Indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride.



(9)

The adduct (8)(20mgm.) was heated in boiling nitrobenzene (5ml.) for 5 minutes. Indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride (9) crystallised from the cooled solution as golden yellow needles, and was recrystallised from chlorobenzene:nitrobenzene (1:1).

Yield: 15 mgm.

M.p.: 357-360°

Analysis: Found; C, 83.1; H, 3.1%

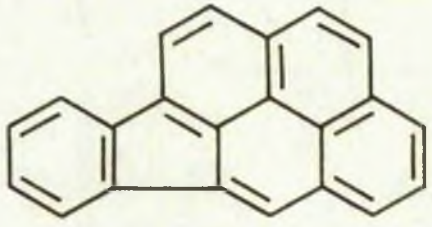
$C_{24}H_{10}O_3$ requires; C, 83.2; 2.9%

Alternatively, on boiling under reflux a solution of indeno[2,1-a]perinaphthene (85mgm.) and maleic anhydride (40mgm.) in nitrobenzene (4ml.) the fully aromatic anhydride (10) was prepared directly.

Yield: 73 mgm.

M.p.: 358-361°

C.II.3. Indeno[1,2,3-cd]pyrene.



(10)

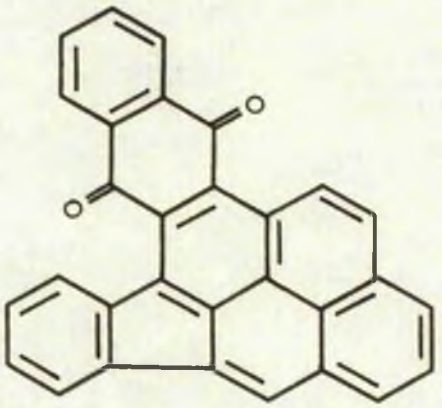
Indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride (9)(73mgm.)

was intimately mixed with an excess of soda lime (4gm.) and the whole was heated strongly in a hard glass tube. Indeno[1,2,3-cd]pyrene (10) sublimed off as canary yellow plates which were taken up in benzene. The benzene solution was chromatographed on a column of alumina (8 x 1.1 cm.) using benzene:petrol (1:10) as developer and eluant, and the product obtained by reducing the eluates to low volume on the water bath. The hydrocarbon in solution displays a greenish yellow fluorescence in daylight and U.V. light.

Yield:	32 mgm.	
M.p.:	162.5-163.5°	
Analysis:	Found;	C, 95.9; H, 4.2%
	$C_{22}H_{12}$ requires;	C, 95.6; H, 4.4%

C,II,4. Reactions of Indeno[2,1-a]perinaphthene with Dienophiles:

with 1:4-Naphthoquinone.

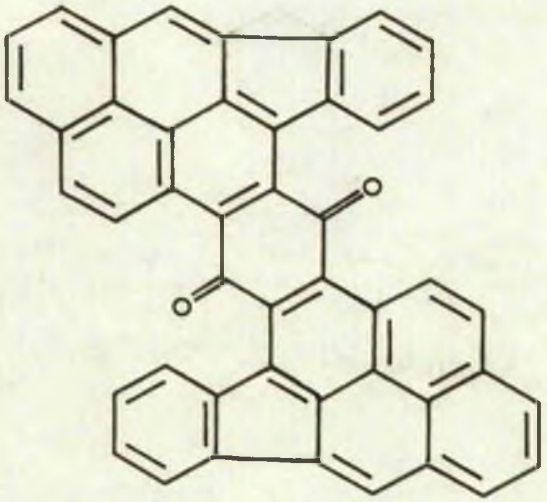


(11)

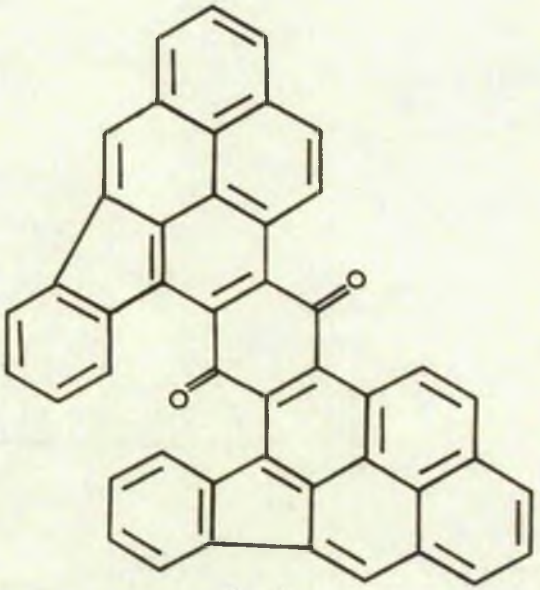
A solution of indeno[2,1-a]perinaphthene (110mgm.) and 1:4-naphthoquinone (70mgm.) in nitrobenzene (5ml.) was boiled for 30 minutes. On cooling the solution precipitated indeno[1,2,3-cd]naphtho-[2',3'-a]pyrene-5:16-quinone (11), subsequently obtained in the form of orange needles on recrystallisation from N:N-dimethylformamide. The quinone gives a greenish-blue vat with alkaline sodium dithionite.

Yield:	120 mgm., (67%)		
M.p.:	263-265°		
Analysis:		Found;	C, 88.7; H, 3.5%
	$C_{30}H_{14}O_2$	requires;	C, 88.1; H, 3.5%

C,II,5. Reactions of Indeno[2,1-a]perinaphthene with Dienophiles: with 1:4-Benzoquinone.



(12)

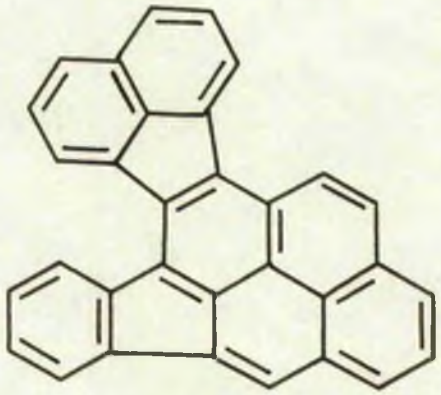


(13)

A solution of indeno[2,1-a]perinaphthene (100mgm.) and 1:4-benzoquinone (45mgm.) in nitrobenzene was boiled for 15 minutes. The product (12 or 13) separated as a microcrystalline solid from the boiling solution, and was subsequently recrystallised from excess nitrobenzene as small orange needles. The quinone gives no vat with alkaline sodium dithionite.

Yield:	90 mgm., (76%)		
M.p.:	Above 400°		
Analysis:		Found;	C, 90.9; H, 3.4%
	$C_{46}H_{20}O_2$	requires;	C, 91.4; H, 3.3%

C.II.6. Reactions of Indeno[2,1-a]perinaphthene with Dienophiles: with 7-Bromoacenaphthylene.



(14)

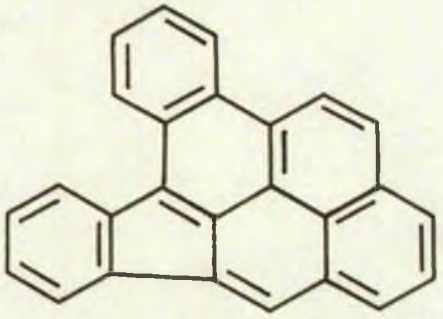
A solution of indeno[2,1-a]perinaphthene (126mgm.) and 7-bromoacenaphthylene (260mgm.) in nitrobenzene (10ml.) was boiled under reflux for 5 minutes. The solution became reddish-brown, and on cooling the product (14) was deposited as dull golden-yellow needles. The adduct (14) was eventually obtained in the form of orange needles by crystallisation from nitrobenzene and subsequently from nitrobenzene:xylene mixture (1:1). A sample was air dried at 120° for 2 hours for analysis.

Yield:	90 mgm., (45%)	
M.p.:	343-346°	
Analysis:	Found;	C, 93.0; H, 4.9%
	$C_{32}H_{16}$ requires;	C, 96.0; H, 4.0%

In an attempt to improve the above analytical data, a sample was sublimed under reduced pressure.

Analysis:	Found;	C, 94.3; H, 3.9%

C.II.7. Reactions of Indeno[2,1-a]perinaphthene with Dienophiles: with Benzyne.



(15)

The procedure used in the preparation of benzyne follows that described (without experimental details) by Wittig[6].

A mixture consisting of indeno[2,1-a]perinaphthene (126mgm.) on the one hand, and o-bromofluorobenzene (2ml.), magnesium (230mgm.) and tetrahydrofuran (10ml.) on the other (sufficient to produce an excess of benzyne with respect to the hydrocarbon) was boiled under reflux for 15 minutes by which time the deep red colour of the substrate had been replaced by an orange colouration. The reaction mixture was treated with an excess of dilute sulphuric acid, and the organic material taken up in ether solution. The latter was washed free of acid, dried over anhydrous potassium carbonate, and the solvent removed by evaporation (eventually under reduced pressure). The residual orange red liquid was dissolved in benzene prior to filtration through a column of alumina (16 x 3.2 cm.) using the latter solvent as developer and eluant. After removal of the bulk of the solvent from the eluates, an orange-red crystalline solid was deposited. The pure product (15) was obtained by recrystallisation from xylene.

The compound (15) gives a violet colouration with concentrated sulphuric acid.

Yield:	24 mgm.	
M.p.:	262-264°	
Analysis:	Found;	C, 95.7; H, 4.4%
	$C_{26}H_{14}$ requires;	C, 95.7; H, 4.3%
M.W.:	Found;	355 (Rast).
	$C_{26}H_{14}$ requires;	326

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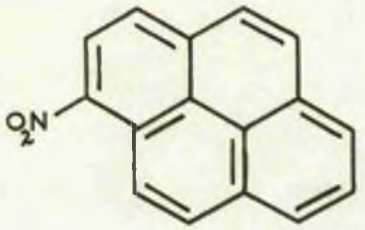
C.III. INDENO[1.2.3-cd]PYRENE: SYNTHESIS FROM PYRENE.

C.III.1. 1-Nitropyrene.



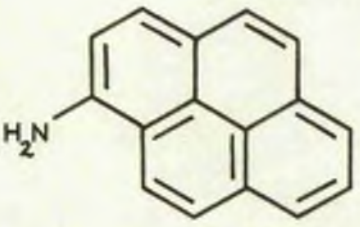
(16)

This and the succeeding preparation are based on the work of Vollmann[4].

Finely powdered pyrene (30gm.) suspended in glacial acetic acid (240ml.) was nitrated by the addition of nitric acid (sp.gr.,1.4) (12.ml.) in acetic acid (15ml.) with stirring at 50° . On cooling the product (16) was deposited, removed by filtration, and after being washed free of acid, was air dried at 110° and used subsequently without further purification.

Yield:	37.9 gm.	(lit.; 44.5 gm.)
M.p.:	150°	(lit.; 150°)

C.III.2. 1-Aminopyrene.

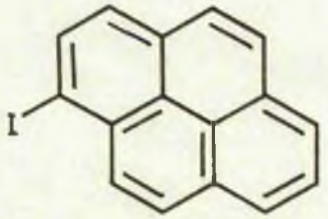


(17)

1-Nitropyrene (35gm.) in boiling ethanol (100ml.) was reduced by the addition of sodium hydrosulphide (22gm.) in water (20ml.) with stirring. The product (17) which crystallised from the cooled reaction mixture was used subsequently without further purification.

Yield:	22.6 gm.,	(lit.; 24.8 gm.)
M.p.:	112-114°	(lit.; 113-115°)

C.III.3. 1-Iodopyrene.



(18)

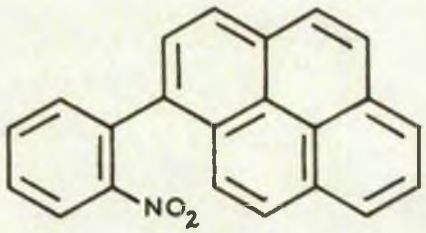
This preparation is based on the work of Lund and Berg[5].

1-Aminopyrene (17)(11.2gm.) suspended in 0.5N sulphuric acid (200ml.) was diazotised by the addition of sodium nitrite (4.5gm.) dissolved in water (75ml.). A solution of potassium iodide (12gm.) in water (75ml.) was then added to the above, which resulted in the formation of a red precipitate which commenced to decompose spontaneously accompanied by the evolution of nitrogen. When the initial reaction had subsided, decomposition was completed by adding copper bronze (10gm.) and heating the resultant mixture on the water bath until the evolution of nitrogen ceased.

Organic material was extracted into benzene, which was washed free of acid with water and dried over anhydrous sodium sulphate. The solution was filtered through a column of alumina (10 x 2.9 cm) whereupon concentration of the eluates afforded 1-iodopyrene(18).

Yield:	5.98 gm.,	(2.5%)
M.p.:	85-86°	(lit.; 88°)

C.III.4. 1-(o-nitrophenyl)Pyrene.



(19)

1-Iodopyrene (18)(2gm.) and o-bromonitrobenzene (1.55gm.) were heated during a period of 3 hours at a temperature of about 210°, during which time copper bronze (4gm.;100% excess) was added in about 20 portions. The reaction mixture, which was agitated by hand to ensure intimate mixing, was mobile at the start of the reaction, but towards the end of it became extremely viscous.

The cooled melt was extracted with benzene and excess copper bronze removed by filtration. The golden yellow extract was evaporated to low volume on the water bath, prior to chromatographing on a column of alumina (15 x 2.5 cm.). Initial development of the column using benzene:petrol (1:4) yielded an almost colourless eluate (300ml.), which fluoresced bright blue under U.V. light and this consisted largely of unreacted 1-iodopyrene. Continued development of the column with benzene:petrol (1:1) yielded golden yellow eluates (ca. 1000ml.) and from this fraction the product (19) was subsequently obtained. Development was concluded using pure benzene. Again golden yellow eluates were obtained, but no quantity of useful product was isolated from the fraction.

The second fraction (above) was concentrated on the water bath, and after the residual oil had been triturated with ethyl acetate 1-(o-nitrophenyl)pyrene (19) crystallised as golden yellow needles m.p., 140-142°. After one crystallisation from ethyl acetate the m.p. was constant at 146.5-147.5° and could not be raised by further recrystallisation.

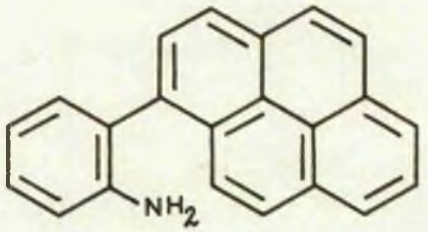
Yield: 0.875 gm., (44.0%)

M.p.: 146.5-147.5°

Analysis: Found; C, 81.7; H, 3.9; N, 4.1%

$C_{22}H_{13}O_2N$ requires; C, 81.7; H, 4.1; N, 4.3%

C,III,5. 1-(o-aminophenyl)Pyrene.



(20)

1-(o-nitrophenyl)Pyrene (0.25gm.), dissolved in A.R. acetic acid (50ml.) was hydrogenated at atmospheric pressure in the presence of 20% palladised charcoal catalyst (100mgm.). Absorption of hydrogen ceased after ca. 1½ hours when the theoretical quantity had been taken up. The original golden yellow solution became colourless and assumed a bright blue fluorescence in U.V. light.

After removal of the catalyst by filtration, the crude amine was precipitated by the addition of the acetic acid solution to excess water, and subsequently taken up in ether. After working up in the usual fashion and removal of solvent on the water bath a brown oil remained which did not crystallise, but slowly decomposed. The amine (20) was used in the next step without subsequent purification and was characterised though its picrate.

Yield: 0.21 gm., (92.6%)

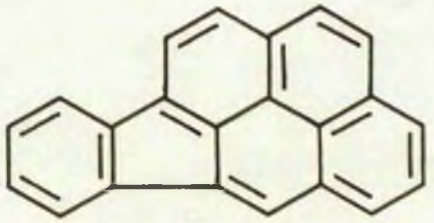
1-(o-aminophenyl)Pyrene and pieric acid in equimolecular proportions were heated together in boiling benzene for 5 minutes. The product, which crystallised on cooling, was recrystallised twice from ethanol to yield the picrate as golden-yellow rhombohedra.

M.p.: 206-207.5°

Analysis: Found; C, 64.0; H, 3.3; N, 10.4%

$C_{28}H_{18}O_7N_4$ requires; C, 64.4; H, 3.5; N, 10.7%

C.III.6. Indeno[1,2,3-cd]pyrene.



(10)

Crude 1-(o-aminophenyl)pyrene (20)(110mgm.) prepared as in (C,III,5.) was heated under reflux in a mixture of glacial acetic acid (2ml.) and sulphuric acid (3ml.) for 5 minutes during which time it partly dissolved. To the cooled mixture was added sodium nitrite (40mgm.) in water (1ml.) in one lot, whereupon a bright red colour developed immediately. After 3 minutes urea was added to destroy the excess of nitrous acid. Copper bronze (1gm.) was added in one lot, the reaction mixture was allowed to stand for 5 minutes and was then heated on the boiling water bath for 10 minutes, the red colour being replaced by a pronounced lemon yellow.

The reaction mixture was filtered to remove excess copper and the residue was extracted with boiling benzene. The lemon yellow filtrate, which possessed a strong fluorescence, was washed successively with water, sodium bicarbonate solution, water and finally dried over anhydrous sodium sulphate. The dried solution was evaporated to low volume on the water bath, and purification was carried out by filtration through a column of alumina (9 x 2.5 cm.) using benzene:light petrol (1:1) as developer and eluant. A bright yellow zone was rapidly removed into the eluates whereas an orange zone was retained on the column. Concentration of the eluates and addition of light petrol resulted in the precipitation

of indeno[1,2,3-cd]pyrene (10) as lemon yellow plates. This compound did not depress the m.p. of the product prepared in (C,I,5.) and the two compounds had identical absorption spectra.

Yield: 39 mgm., (38%)

M.p.: 161.5-163°

Analysis: Found; C, 95.8; H, 4.1%

$C_{22}H_{12}$ requires; C, 95.6; H, 4.4%

The picrate was prepared by heating together equimolecular quantities of the hydrocarbon and picric acid in ethanol. The complex crystallised as red elongated needles, but it did not possess a sharp melting point.

M.p.: 150-180°

Analysis: Found; C, 66.3; H, 3.2; N, 8.4%

$C_{22}H_{12}C_6H_3O_7N_3$ requires; C, 66.5; H, 3.0; N, 8.3%

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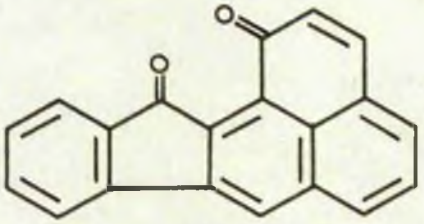
C.IV. BEHAVIOUR OF INDENO[2,1-a]PERINAPHTHENE ON OXIDATION AND REDUCTION.

C.IV.1. Oxidation of Indeno[2,1-a]perinaphthene with Chromic Acid.



(21)

A.R. chromium trioxide (100mgm.) was added to a suspension of indeno[2,1-a]perinaphthene (6)(126mgm.) in A.R. glacial acetic acid (20ml.) and the mixture was boiled under reflux for 2 minutes. A further quantity of A.R. chromium trioxide (100mgm.) was added and the mixture was boiled under reflux for another minute, after which it was added to an excess of water whereupon an orange yellow solid was precipitated. The precipitated solid was subsequently taken up in chloroform, and the chloroform solution was washed successively with water, sodium bicarbonate solution and water and finally dried over sodium sulphate. The chloroform solution was evaporated to low volume on the water bath and chromatographed on a column of alumina using chloroform:benzene (1:1) as developer and eluant. Evaporation of the orange eluates to low volume gave an orange red solid, which on subsequent crystallisation from N:N-dimethylformamide precipitated the quinone (21;suggested formula) in the form of orange needles.

The quinone gives a violet-blue vat readily with alkaline sodium dithionite and a greenish yellow colour with concentrated sulphuric acid.

Yield:	52 mgm.	
M.p.:	283–285°	
Analysis:	Found;	C, 85.0; H, 3.7%
	$C_{20}H_{12}O_2$ requires;	C, 85.1; H, 3.6%

After recrystallisation from N:N-dimethylformamide (twice) and then chlorobenzene (twice) the compound had constant m.p.

C.IV.2. Oxidation of Indeno[2,1-a]perinaphthene with Lead Tetra-acetate.

Lead tetra-acetate (1.8gm.; large excess) was added to a solution of indeno[2,1-a]perinaphthene (200mgm.) in benzene (50ml.) at 15° and the mixture allowed to stand for 1 hour. At this point, there remained only a negligible quantity of starting material as shown by attempted extractions of small portions of the mixture using 78% sulphuric acid. The deep crimson red reaction mixture was poured into an excess of water and the precipitated lead dioxide removed by filtration. The filtrate was washed with water, dried over anhydrous sodium sulphate, and the solvent removed on the water bath. The residue in benzene was chromatographed on a column of alumina (9 x 2.7 cm.) and on development and elution with benzene a crimson zone rapidly passed down the column. This fraction in benzene remained inert to attempted extraction with sodium hydroxide solution, and only a negligible quantity was extracted using 78% sulphuric acid. On concentration of this solution and crystallisation from benzene:ethanol (1:2) a product was obtained as black needles. Recrystallisation from benzene:ether (10:1) yielded a product in small violet black needles which did not depress the m.p. of the violet black product (7) obtained in (C,I,5.) and both products had identical absorption spectra in the range 350–650mμ.

Continued elution of the column using ether and finally methanol yielded no useful material.

Yield: 50 mgm.

M.p.: 293-296°

C.IV.3. Acetoxylation of Di(indeno[2,1-a]perinaphthenyl).

Lead Tetra-acetate (1gm.) was added to a solution of di(indeno[2,1-a]perinaphthenyl)(7)(100mgm.) in dry benzene (50ml.) and the resulting mixture was boiled under reflux for 2 hours. The cooled reaction mixture was poured into water and extracted with ether. The ether extract was washed thoroughly with water, dried over anhydrous sodium sulphate and the solvent removed on the water bath. The residue was taken up in benzene and chromatographed on a column of alumina (10 x 2.7 cm.). The column was developed with benzene and subsequently eluted with benzene:ether (1:1), a green zone coming through fairly rapidly. Concentration of the eluates gave the mono-acetoxy derivative of (7) in black needles which was recrystallised from xylene.

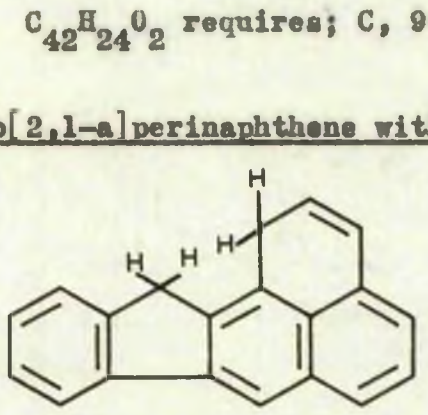
Yield: 30 mgm.

M.p.: greater than 360°.

Analysis: Found; C, 90.4; H, 4.1%

$C_{42}H_{24}O_2$ requires; C, 90.0; H, 4.3%

C.IV.4. Reduction of Indeno[2,1-a]perinaphthene with Zinc and Acetic Acid.



(22)

Indeno[2,1-a]perinaphthene (6)(0.5gm.) was heated in boiling A.R. acetic acid (100ml.) and zinc dust (10gm.; large excess) was added in portions during the course of 15 minutes. The original crimson red solution became pale pink with a blue fluorescence during the course of the addition. The reaction mixture was poured into an excess of water,

and the product taken up in ether. The ether solution was washed with water, sodium bicarbonate solution and water, and finally dried over sodium sulphate. The solvent was removed by distillation on the water bath, and the product (22; suggested formula) obtained as almost colourless plates from benzene:ethanol (2:5)(note 1).

Yield: 0.461 gm., (91.0%)

M.p.: 169.5-171.5° (decomp.)

Analysis: Found; C, 94.3; H, 5.4%

$C_{20}H_{14}$ requires; C, 94.5; H, 5.55%

On refluxing the mother liquors from above with sym-trinitrobenzene and subsequent cooling, a complex separated and was obtained as an orange red microcrystalline solid on recrystallisation from ethanol. Under the microscope the complex consisted of aggregates of orange-red, flat needles.

M.p.: 135-137°

Analysis: Found; N, 12.6%

$C_{20}H_{14}.\ 2(C_6H_3O_6N_3)$ requires; N, 12.35%

Note 1. Further purification by way of recrystallisation failed to remove the colour of the crystals which were always tinted brown. The hydrocarbon in organic solvents gives solutions possessing a light-green fluorescence and in sulphuric acid an intense greenish yellow fluorescence which becomes dark green on standing.

C.IV.5. Dihydro-indeno[2,1-a]perinaphthene: Action of Osmium Tetroxide.

Dihydro-indeno[2,1-a]perinaphthene (22)(200mgm.) in benzene (5ml.) (note 1) was treated with osmium tetroxide (200mgm.; 1 mole). After both reactants had gone into solution, pyridine was added (0.2ml.), whereupon a brown solid started to precipitate out at once, and the reaction appeared to be complete after 15 minutes had elapsed. The mixture was allowed to stand for a total of 18 hours to ensure complete

reaction, the brown precipitate then being filtered off and washed with a little benzene.

The filtrates from above, which were crimson red in colour, were washed with water, dilute sulphuric acid (to remove pyridine), water and subsequently dried over anhydrous sodium sulphate. The solvent was entirely removed and the brownish residue taken up in benzene. The solution was subsequently extracted with 77% sulphuric acid (sulphuric acid:water - 2:1), the extracts possessing a deep green colour. The acid extracts were diluted with an excess of crushed ice and water. The precipitated brown solid was taken up in ether and the ether solution was worked up in the usual manner. The residue obtained, after removal of ether, was dissolved in benzene, and the benzene solution chromatographed on alumina (4.0 x 2.7 cm.) using benzene as developer and eluant. A crimson-red zone came through rapidly and on evaporation of the eluates to low volume the product crystallised as reddish-brown leaflets whose m.p. was not depressed on admixture with an authentic sample of indeno[2,1-a]perinaphthene (6).

Yield:	24 mgm.
M.p.:	210-211°

An insoluble brown solid (370mgm.) obtained in the above reaction was shaken with methylene dichloride (50ml.) and water (50ml.) containing potassium hydroxide (0.5gm.) and mannitol (5gm.) for 60 hours, but the colour of the two layers remained practically unaltered and the solid remained suspended.

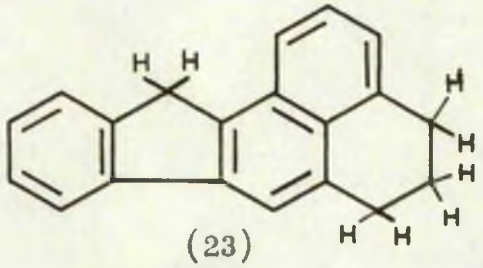
Note 1. The benzene was specially purified as follows. A.R. benzene was boiled under reflux for 3 hours over aluminium chloride, and the bulk of the solvent recovered by distillation. The distillate was washed successively with water, sodium bicarbonate solution(several times), and water, and dried over anhydrous sodium sulphate. Finally, the benzene was fractionally distilled over sodium wire, and eventually stored over sodium wire.

C,IV,6. Dihydro-indeno[2,1-a]perinaphthene: Attempted Catalytic Hydrogenation with Palladised Charcoal.

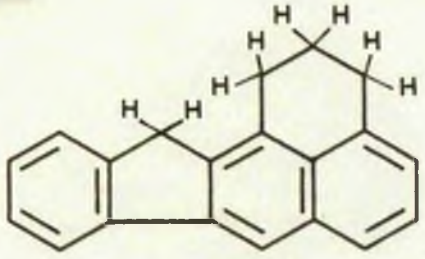
Dihydro-indeno[2,1-a]perinaphthene (450mgm.) in acetic acid (125ml.) was subjected to hydrogenation at atmospheric pressure using 20% palladised charcoal (100mgm.) as catalyst. No uptake was observed over 1 hour, but the pale pink solution rapidly assumed a crimson-red colour. Subsequently the solution was boiled under reflux with the catalyst in the presence of atmospheric oxygen for 15 minutes. After removal of catalyst the acid solution was added to an excess of water, and the precipitated organic material taken up in benzene solution. The latter was washed free of acid and dried over anhydrous sodium sulphate prior to chromatography on a column of alumina (9 x 2.5 cm.). On development and elution with benzene, a crimson-red zone rapidly passed down the column, and the resulting red eluates were concentrated to low volume. Addition of petrol resulted in the precipitation of the product in reddish-brown needles which on admixture with an authentic sample of indeno[2,1-a]perinaphthene (6) did not depress the m.p. of the latter.

Yield: 254 mgm., (57%)

C,IV,7. Tetrahydro-indeno[2,1-a]perinaphthene.



(23)



(24)

Dihydro-indeno[2,1-a]perinaphthene (22)(500mgm.) in glacial acetic acid (200ml.) was subjected to hydrogenation at atmospheric pressure in the presence of Adam's platinium oxide catalyst (250mgm.). The reduction appeared complete after 6 hours. The solution, which was originally pale red in colour and exhibited a light blue fluorescence,

became colourless as the reduction progressed and ceased to fluoresce.

The hydrogenated material was taken up in ethereal solution from which acetic acid was removed by washing. Following evaporation of the solvent, the residue was distilled under reduced pressure (ca. 1mm.) at 200° in a suitable sublimation tube to yield a pale orange oil which solidified to a glass at room temperature. The product (note 1) was obtained in the form of almost colourless plates by crystallisation from either acetic acid or ethanol (note 2).

Yield: Almost quantitative in several experiments.

M.p.: 106–117.5°

Analysis: Found; C,92.7; H, 7.1%

$C_{20}H_{16}$ requires; C, 93.7; H, 6.3%

A sym-trinitrobenzene complex of (23; 24) was obtained by boiling a solution containing equimolar proportions of the reactants under reflux for 5 minutes. The complex was obtained in the form of orange needles by recrystallisation from ethanol, and did not have a sharp m.p. but softened slowly over a range without decomposition.

M.p.: 137.5–155.5°

Analysis: Found; C,66.6; H, 4.6; N, 9.28%

$C_{26}H_{19}N_3O_6$ requires; C, 66.5; H, 4.1; N, 8.96%

A 2:4:7-trinitrofluorenone complex of (23; 24) was prepared by boiling under reflux for 5 minutes an ethanolic solution containing equal weights of the reactants. The complex was obtained in the form of small pink needles by recrystallisation from acetic acid.

M.p.: 221–223° (softens slowly with sublimation over the range 213–221°)

Analysis: Found; C, 69.2; H, 3.8; N, 7.4%

$C_{33}H_{21}O_7N_3$ requires; C, 69.3; H, 3.7; N, 7.3%

Note 1. Notwithstanding the melting point range and poor analytical data recorded above, the identification of the product as either of the two tetrahydro-indeno[2,1-a]perinaphthenes (23) or (24) or a mixture thereof has been made on the basis of the comparison of the U.V. absorption spectrum with that of 1:2-benzfluorene (plate VII) and 2:3-benzfluorene (plate VI).

Note 2. Repeated crystallisation of the product from either of these solvents resulted in no significant improvement in the melting point or analytical data. Crystallisation from petrol gave a compound with even less satisfactory properties.

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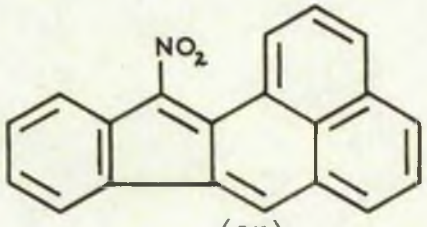
C.V. ELECTROPHILIC SUBSTITUTION OF INDENO[2,1-a]PERINAPHTHENE.

C.V.1. Nitroindeno[2,1-a]perinaphthene.

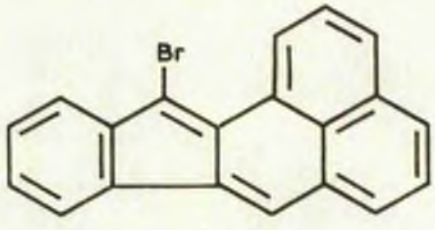


(25)

Tetranitromethane (98mgm.) in absolute ethanol (2ml.) was added to a solution of indeno[2,1-a]perinaphthene (6)(126mgm.) in pure dry pyridine (5ml.). The initially crimson-red solution assumed a purple-violet colour rapidly. The solution was kept at room temperature (15°) for 5 minutes, and then diluted with excess ether (ca. 250ml.). The ether solution was washed first with dilute hydrochloric acid to remove nitroform and pyridine, then with water and sodium bicarbonate solution, and finally dried over sodium sulphate. The ether was removed on the water bath, and the residue was chromatographed on alumina using pure ethyl acetate as solvent and developer. On concentration to low volume, the violet eluates afforded the nitro derivative (25; suggested formula) as violet prisms.

Yield:	22 mgm.	
M.p.:	186-190° (decomp.)	
Analysis:	Found;	C, 81.5; H, 3.5; N, 4.8%
	$C_{20}H_{11}O_2N$ requires;	C, 80.8; H, 3.7; N, 4.7%

C.V.2. Bromoindeno[2,1-a]perinaphthene.



(26)

Bromine (350mgm.) carried as vapour in dry nitrogen was passed through a solution of indeno[2,1-a]perinaphthene (6)(500mgm.) in A.R. carbon tetrachloride (100ml.) during 30 minutes. Reaction was accompanied by the vigorous evolution of hydrogen bromide. At the end of the bromination, the solution was washed thoroughly with water, and then dried over sodium sulphate prior to the removal of the solvent under reduced pressure on the water bath.

The residual red solid was taken up in dry benzene and filtered through alumina (9 x 2.5 cm.) using benzene as developer and eluant. On concentration of the eluates to low volume, the mono-bromo derivative (26; suggested formula) crystallised as reddish-brown plates.

Yield: 489 mgm., (74.5%)

M.p.: 177.5-178.5° (the compound showed slight softening between 162° and 177.5° followed by rapid melting accompanied by gas evolution.)

Analysis: Found; C, 72.2; H, 3.4; Br. 24.1%

$C_{20}H_{11}Br$ requires; C, 72.5; H, 3.35; Br. 24.1%

Equimolecular proportions of bromoindeno[2,1-a]perinaphthene and 1:3:5-trinitrobenzene were dissolved in benzene and heated under reflux for 5 minutes. On cooling, the complex was precipitated as black needles, subsequently recrystallised from ethanol.

M.p.: 201-209° (decomp.)

Analysis: Found; C, 57.3; H, 2.5; N, 7.8%

$C_{26}H_{14}N_3O_6Br$ requires; C, 57.4; H, 2.6; N, 7.7%

C.V.3. Pyrene-11:12-dicarboxylic Acid: Preparation from Bromoindeno[2,1-a]perinaphthene.

A solution of bromoindeno[2,1-a]perinaphthene (80mgm.) and maleic anhydride (30mgm.) in nitrobenzene (7ml.) was boiled for 5 minutes (note 1). On cooling, the product (9) crystallised in golden-yellow needles which

was subsequently recrystallised from nitrobenzene.

Yield: 75 mgm., (90%)

M.p.: Above 350°

Analysis: Found; Br. 1.09%(note 2).

Note 1. At the conclusion of the period of heating under reflux, a few drops of vapour were distilled off and condensed in liquid air. The condensate was shaken with water and on separation from the nitrobenzene later, the aqueous phase was shown to give an instantaneous precipitate with silver nitrate.

Note 2. This analysis indicates that there is 5.8% of brominated product present resulting from the presence in the original starting material of an isomer brominated in a position other than the 1 or 12.

Note 3. In view of the apparent inhomogeniety of the product resulting from the bromination of (6), an attempt was made to obtain a homogeneous sample by fractional crystallisation of the sym-trinitrobenzene complex of bromoindeno[2,1-a]perinaphthene. Recrystallisation of the latter (five times) from ethanol did not produce any significant improvement, as evidenced by conversion of the purified material to (9).

C,V,4. Indeno[1,2,3-cd]pyrene: Preparation from Bromoindeno[2,1-a]-perinaphthene.

Indeno[1,2,3-cd]pyrene-11:12-dicarboxylic anhydride (206mgm.) prepared as in (C,V,3.) was intimately mixed with soda lime (10gm.) and the mixture heated strongly. Indeno[1,2,3-cd]pyrene (10) sublimed out, and the cold sublimate was taken up in benzene. After concentration of the benzene solution and addition of petrol, the product crystallised in the form of bright yellow plates.

Yield: 115 mgm., (70%)

M.p.: 153-160°

Analysis: Found; Br. 1.28%(note 1).

Note 1. This represents 5.7% of brominated compound in the product.

C,V,5. Indeno[1,2,3-cd]pyrene prepared from Bromoindeno[2,1-a]perinaphthene: Debromination.

Indeno[1,2,3-cd]pyrene (10; C,V,4.)(100mgm.) was dissolved in ethanol (125ml.) and 25% aqueous sodium hydroxide was added until the resulting boiling solution became almost saturated with respect to the hydrocarbon, a little ethanol being added to prevent its precipitation. Raney nickel:aluminium alloy (10gm.) was added to the boiling solution during the course of 30 minutes, after which the metal residue was filtered off and washed with boiling ethanol. The filtrates were concentrated to low volume and added to an excess of water. The precipitated product was taken up in ether and the ether solution washed successively with water, sodium bicarbonate solution and water, and dried solvent removed on the water bath. The yellow microcrystalline residue was recrystallised from benzene:light petrol (1:1) to give indeno[1,2,3-cd]-pyrene (10) as yellow plates which did not depress the melting point of the product from (C,III,6.) when admixed with it.

Yield:	82.5 mgm.	
M.p.:	160.5-162.5°	
Analysis:	Found;	C, 95.4; H, 4.35%
	$C_{22}H_{12}$ requires;	C, 95.6; H, 4.4%

C,V,6. Oxidation of Bromoindeno[2,1-a]perinaphthene: with Chromic Acid.

A suspension of bromoindeno[2,1-a]perinaphthene (150mgm.) was heated in a boiling solution of chromic anhydride (325mgm.) in glacial acetic acid (7ml.) for 5 minutes. The reaction mixture was poured into an excess of water, and the precipitated solid dissolved in chloroform. The chloroform solution was washed successively with water, 10% aqueous sodium hydroxide, water and eventually dried over anhydrous sodium

sulphate. After concentration on the water bath, the solution was chromatographed on a column of alumina (9 x 2.5 cm.) using chloroform as developer and eluant. After removal of chloroform on the water bath, the dark orange microcrystalline residue was crystallised from chlorobenzene to yield the impure quinone (21; suggested formula)(note 1) in the form of small orange plates.

Yield:	15 mgm., (11.7%)
M.p.:	275–280° (softened slowly over range 244–275°).
Analysis:	Found; Br., 1.67%

Note 1. Corresponds to ca. 7.6% of brominated quinone.

C,V,7. Bromoindeno[2,1-a]perinaphthene: Action of Boiling Nitrobenzene.

A solution of bromoindeno[2,1-a]perinaphthene 1:3:5-trinitrobenzene complex (40mgm.) in nitrobenzene (5ml.) was boiled for 5 minutes, and the cooled solution made up to 50 ml. with benzene. The benzene solution was exhaustively extracted (4 times) with 86% sulphuric acid(note 1). The benzene solution became almost colourless at the end of the extraction. On diluting the dark green acid solution with ice and water, the precipitated solid, after being dissolved in benzene and filtered through alumina, assumed the crimson-red colour of bromoindeno[2,1-a]perinaphthene.

Note 1. This acid concentration i. e., 86%, though greater than that required for the quantitative extraction of indeno[2,1-a]perinaphthene, does not extract any di(indeno[2,1-a]perinaphthenyl).

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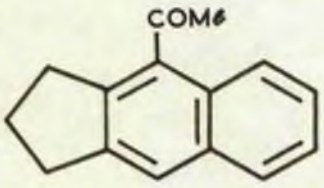
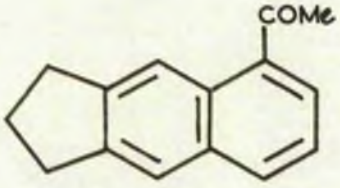
C,VI. cycloPENTA[a]PERINAPHTHENE: ATTEMPTED SYNTHESIS.

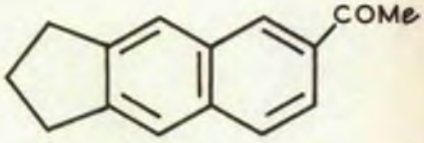
C,VI,1. Acetyl-2:3-cyclopentenonaphthalene.



(27)



(28)



(29)

Acetyl chloride (26.6gm., 24ml.) and powdered anhydrous aluminium chloride (46gm.) dissolved in methylene dichloride (250ml.) were added to a vigorously stirred solution of 2:3-cyclopentenonaphthalene (note 1) (57gm.) in methylene dichloride (250ml.) at room temperature during the course of half an hour. The reaction mixture was stirred at room temperature for a further 2 hours and then decomposed by addition to an excess of crushed ice and water. The product was worked up in the usual manner. Distillation yielded a straw coloured viscous oil at 152-156°/ 1.0 mm.

On standing at room temperature, a quantity of colourless crystalline material precipitated spontaneously from the oil during the course of 3 days. Thereafter the bulk of the precipitate showed no apparent increase, even if permitted to stand for a period of up to 6 weeks. Removal of the solid was achieved by trituration of the mixture with light petrol followed by filtration. The precipitate was washed with a further small volume of light petrol (note 3).

The combined oil, filtrate and washings were concentrated to remove solvent, and the residue on distillation yielded a colourless oil at 156-160°/1 mm.(note 2).

Yield:	45.0 gm. , (63%)	
M.p.:	156-160°/1 mm.	
Analysis:	Found;	C, 85.8; H, 6.8%
	$C_{15}H_{14}O$ requires;	C, 85.7; H, 6.7%

A 2:4-dinitrophenylhydrazone, elongated orange prisms from N:N-dimethylformamide, was prepared by warming together equimolecular proportions of the oil obtained as above and 2:4-dinitrophenylhydrazone in ethanol together with a catalytic quantity of hydrochloric acid.

M.p.: 289-291°

Analysis: Found; C, 64.5; H, 5.0; N, 14.2%

$C_{21}H_{18}O_4N_4$ requires; C, 64.6; H, 4.6; N, 13.35%

Note 1. 2:3-cyclopentenonaphthalene was prepared by the catalytic dehydrogenation, using palladised charcoal, of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38; C,VII,4.).

Note 2. As a consequence of the results obtained in (C,VI,3.), it would appear that the oily fraction from this reaction consists of a mixture of (27) and (28). The dinitrophenylhydrazone obtained presumably corresponds to that ketone which is a major component of the mixture.

Note 3. The crude precipitate was obtained pure in the form of colourless plates by crystallisation from acetone:petrol (1:10). The constitution of this ketone has been tentatively established as (29) on account of the failure of the corresponding oxymethylene ketone to undergo cyclodehydration to a perinaphthenone.

Yield: 2.3 gm.

M.p.: 96.5-98°

Analysis: Found; C, 85.3; H, 6.15%

$C_{14}H_{15}O$ requires; C, 85.7; H, 6.7%

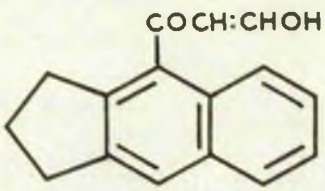
The dinitrophenylhydrazone of this ketone was prepared by heating together equimolecular quantities of the reactants in ethanol in the presence of a catalytic quantity of hydrochloric acid. This derivative was obtained in the form of orange needles by crystallisation from N:N-dimethylformamide.

M.p.: 294-295°

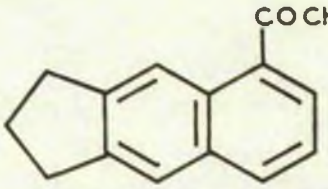
Analysis: Found; C, 65.0; H, 4.6; N, 14.4%

$C_{21}H_{18}O_4N_4$ requires; C, 64.6; H, 4.6; N, 14.35%

C,VI,2. Oxymethylene Derivative of Acetyl-2:3-cyclopentonaphthalene.



(30)



(31)

Ethyl formate (16.68gm.; 18.2ml.; 10% excess) in sodium dried ether (25ml.) was added to a stirred suspension of anhydrous potassium methoxide (15.8gm.; 10% excess) in a solution of acetyl-2:3-cyclopentenonaphthalene (C,VI,1.; note 2)(43gm.) in sodium dried ether at room temperature during the course of 15 minutes. A heavy brown oil began to precipitate almost immediately, and after the addition was complete, the reaction mixture was stirred for a further 2 hours. The resulting potassium salt of the oxymethylene derivative (30 and 31) was taken up in an excess of warm water (note 1). Acidification of the latter with an excess of 4N sulphuric acid generated the free ketone (30 and 31) which was dissolved in ether and processed in the usual manner. Removal of the solvent by evaporation gave the product as a yellow oil (note 2). The latter was cyclodehydrated as detailed in (C,VI,3.) without further purification.

Yield: 40 gm., (82%)

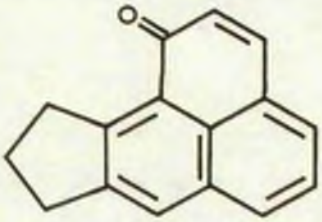
Note 1. The potassium salt dissolved only very slowly in the cold, and it was necessary to use warm water to effect solution. In addition the supernatant ether solution, from which the oily product had separated, was extracted with 10% potassium hydroxide, and the extract added to aqueous solution.

Note 2. In an attempt to obtain the free oxymethylene ketone in a crystalline state, carbon tetrachloride (40ml.) was added to the latter and the whole cooled to -20° to -30°. A small quantity of pale yellow crystalline material (0.98gm.)did separate out, and this was removed by

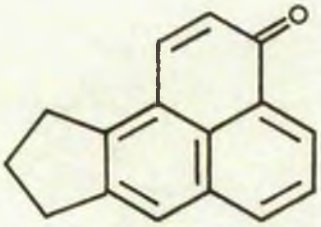
filtration. The bulk of the material, which did not crystallise, was recovered as a yellow oil by evaporation of the solvent.

The separated crystalline material was shown to be identical with oxymethylene 7-acetyl-2:3-cyclopentenonaphthalene (48; C,VII,19).

C,VI,3. cyclopentenoperinaphthenone.



(32)



(33)

A cold solution of sulphuric acid (600ml.) in water (140ml.) was added to a vigorously stirred solution of the oxymethylene ketone from 2:3-cyclopentenonaphthalene (C,VI,2)(40gm.) in carbon tetrachloride (500ml.) at room temperature during the course of 10 minutes. The reaction mixture assumed a reddish-brown colour and became viscous. After the addition of sulphuric acid was complete, stirring was continued for a further 80 minutes, at which point the reaction mixture was poured onto an excess of crushed ice and water (ca. 6 litres). The whole was extracted with carbon tetrachloride (ca. 3 litres) and after filtration to remove organic debris, the extract was washed successively with water, 10% potassium hydroxide solution (thrice), water (twice), and finally dried over anhydrous potassium carbonate. The solvent was removed by evaporation and the residue, a brownish oil, was dissolved in benzene (1 litre). The latter was exhaustively extracted with concentrated hydrochloric acid (note 1)(500ml. portions) until the extracts, originally deep orange-red, possessed only a faint yellow colouration. The acid extracts were successively washed with benzene, filtered to remove organic debris, and diluted with an excess of water. The organic material was precipitated partly as a yellow oil, which dissolved in ether, and

partly as a brown gum, which proved insoluble in the latter. The ether solution was washed free from acid, dried over anhydrous potassium carbonate, and the ether removed by evaporation.

Considerable difficulty attended attempts to obtain crystalline material from the residual brown oil obtained above (note 2). It appeared that a mixture of perinaphthenones (32) and (33) had resulted, presumably by cyclodehydration of the two oxymethylene derivatives derived from ketones (27) and (28). One component appeared thermally unstable, and distillation under reduced pressure resulted in its complete removal, giving a golden-yellow oil (14.5gm.). A homogeneous crystalline product was obtained from the above by crystallisation from absolute methanol (5 volumes to 1 volume of distillate) which gave a perinaphthenone:methanol complex. The perinaphthenone (note 3) was obtained in the form of yellow needles by recrystallisation of the complex from petrol.

Yield:	9 gm., (24.5%)	
M.p.:	79.5-81.5°	
Analysis:	Found;	C, 86.8; H, 5.3%
	$C_{16}H_{12}O_2$ requires;	C, 87.2; H, 5.5%

Note 1. This extraction process makes use of the solubility of perinaphthenones in concentrated hydrochloric acid described in (A,IV,3).

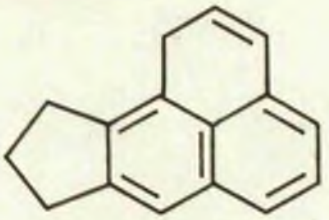
Note 2. This oil was dissolved in boiling petrol, but on cooling, deposition of a gum on the sides of the vessel invariably took place. The gum was partly soluble in the boiling mother liquors, and by decanting the latter from the insoluble residue, a further attempt at crystallisation was made. Only by repetition of this process, and by maintaining gradual cooling of the solution, was it possible to obtain a crystalline deposit.

All the residual gums, which had precipitated from solutions of the ketone, were extracted with boiling petrol and these extracts were combined with mother liquors from the successful crystallisation and filtered

through a column of alumina to remove polymeric material. By careful concentration, cooling and 'seeding' with the crystalline deposit obtained above was it possible to prepare further quantities of crystalline ketone. Inevitably further deposition of gums resulted in cases where 'seeding' was unsuccessful, and such gum could be processed again to yield more crystalline material.

The product obtained in this manner proved inhomogeneous, melting over the range 66–75°. In an attempt to resolve the mixture, fractional crystallisation from methanol (thrice) and finally from petrol gave a product which melted over the slightly elevated range of 67–79°. It was concluded that the major product was contaminated with a tenacious impurity, presumably an isomer. The successful removal of this isomer could only be achieved by distillation under reduced pressure.

C,VI,4. cyclopentenoperinaphthene.



(34)

Lithium aluminium hydride (2gm.) and sodium dried ether (300ml.) were placed in a flask to which was attached a soxhlet extractor containing cyclopentenoperinaphthenone (C,VI,3.; m.p., 79.5–81.5°) (6.3gm.). Air in the apparatus was displaced by a current of oxygen-free nitrogen, which was maintained throughout the duration of the reaction and the subsequent period of heating. On boiling the ether under reflux at a moderate rate, the ketone was continuously extracted and by this means added portionwise to the reaction mixture in the flask. As each addition occured, a spontaneous reaction set in as evidenced by the attendant vigorous ebullition of the ether. All the ketone was transferred in this manner during the course of 40 minutes, whence an

almost white precipitate of the reaction complex was deposited. The reaction mixture was boiled under reflux for a further 15 minutes, and then added to an excess of ice cold dilute hydrochloric acid (note 3) to decompose all the metal-organic complex. The liberated organic material was taken up in ether to give a pale yellow solution, which was subsequently washed with water, 5% sodium hydroxide solution (note 1), water and finally dried over anhydrous sodium sulphate.

The ether was taken off by boiling, and final traces were removed by the addition of petrol, followed by evaporation to dryness. The residual orange oil was taken up in a light petrol:benzene mixture (4:1) prior to chromatography on a column of alumina (15 x 2.3 cm.). On development and elution with petrol, a colourless product was rapidly removed from the column whose presence was recognised by the purple-blue fluorescence (U.V. or daylight) of the eluates. After elution of this product was complete (ca. 500ml. of eluates)(note 2), the solvent was removed by evaporation on the water bath. The residual pale yellow-brown oil crystallised in the form of colourless prisms on standing. This product (note 3) was considered sufficiently homogeneous on the basis of its ready tendency to crystallise in spite of the low m.p., and the ready formation of the sym-trinitrobenzene complex, which is obtained pure directly (see below), to warrant no further purification.

Yield:	4.57 gm., (77.5%)		
M.p.:	78-82°		
Analysis:	Found;	C, 93.3;	H, 6.9%
	$C_{16}H_{14}$ requires;	C, 93.15;	H, 6.85%

Equimolar quantities of the above product (note 3) and sym-trinitrobenzene dissolved in ethanol:benzene mixture (5:1) were heated under reflux for 5 minutes. On cooling the complex was deposited in the form of flat orange needles, whose m.p. was unchanged on further crystallisation. The colour of the T.N.B. complex is consistent with the formulation of the hydrocarbon component as a perinaphthene.

M.p.: 130–132° (decomp.)

Analysis: Found; C, 62.9; H, 4.2; N, 10.3%

$C_{16}H_{14}C_6H_3O_6N_3$ requires; C, 63.0; H, 4.1; N, 10.05%

Note 1. The alkaline extract was observed to be pale orange in colour but acidification gave no useful product.

Note 2. At this point elution was continued with ether, which resulted in dissolution of yellow material which had been retained in an orange band on the column. A pale orange zone remained after the eluates became colourless (ca. 400ml.), and at this stage the column was discarded. Removal of the solvent by evaporation gave a dark brown oil (1.29gm.), which failed to crystallise.

Note 3. The formula (34) represents only one of a number of possibilities for the structure of the resultant cyclopentenoperinaphthene from this reaction. Structural proof, from degradation studies, has not been attempted owing to the restricted quantities of material available.

In an identical preparation, which differed only in that the metal-organic complex was decomposed by ammonium chloride solution as opposed to dilute hydrochloric acid, an inhomogeneous product was obtained. Thus the resultant hydrocarbon (3.3gm.), which was obtained by crystallisation from a small volume of petrol, melted initially over the range 36–44°. After two recrystallisations from petrol this was altered to 58–75°. Doubtless the use of acid in the former preparation is of significance in the generation of only one perinaphthene (see A,IV,7).

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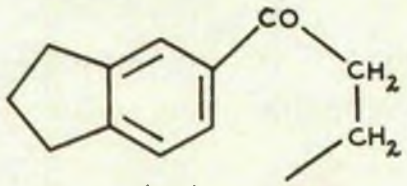
C,VII. cycloPENTA[a]PERINAPHTHENE:
THE ISOMERIC 2:3-cycloPENTENONAPHTHALENE CARBOXYLIC ACIDS.

C.VII.1. Ethyl γ-Keto-γ-(5-indanyl)butyrate.



(35)

This and the succeeding two preparations, (C,VII,2) and (C,VII,3), are based on the work of Robinson[7] as modified by Keller[8].

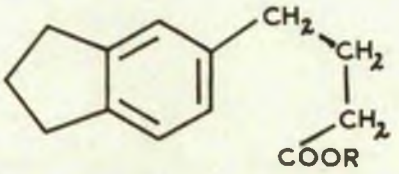
A finely powdered suspension of aluminium chloride (230gm.) and succinic anhydride (116gm.) in nitrobenzene (300ml.) was added to a well-stirred solution of indane (100gm.) in nitrobenzene (600ml.) during the course of 2 hours at room temperature. Stirring was continued for a further 6 hours at room temperature, whereafter the reaction mixture was permitted to stand overnight. After treatment with an excess of 5N hydrochloric acid to decompose the metal-organic complex, the nitrobenzene solution was washed free of acid with water. Nitrobenzene was removed by steam distillation (8 hours; ca. 10 litres of distillate), and the residual brown crystalline mass of crude acid (35; R = H) was dried over phosphorus pentoxide under reduced pressure at room temperature.

A solution of the latter in ethanol (500ml.) containing conc.sulphuric acid (15ml.) was boiled under reflux for 6 hours in order to effect esterification. The crude product was processed in the usual manner, and the ester (35; R = C_2H_5) was obtained as a colourless oil by distillation under reduced pressure, b.p., 172°/10 mm., (lit.; 140-152°/0.03 mm.).

Yield: 148 gm., (lit.; 160gm., 77%)

M.p.: 49-50° (lit.; 50-51°)

C,VII,2. Y-(5-indanyl)Butyric Acid.

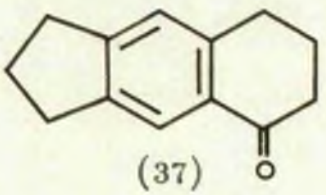


(36)

A mixture consisting of a solution of ethyl Y-keto-Y-(5-indanyl)butyrate (35; R = C_2H_5) (42gm.) in toluene (65ml.) and conc. hydrochloric acid (130ml.) together with zinc wool (85gm.) amalgamated in the usual manner was boiled under reflux for 48 hours, in the course of which a further 3 portions of conc. hydrochloric acid (20ml. in each) were added, and the zinc dissolved completely. The organic phase was washed free of acid, and after removal of solvent by distillation, the residual ester (36; R = C_2H_5) was dissolved in methanol (250ml.) containing sodium hydroxide (15gm.), and the resulting solution boiled under reflux for 2½ hours to effect hydrolysis. The reaction mixture was processed in the usual manner, and the acid obtained as a colourless oil by distillation under reduced pressure, b.p., 148-150°/0.7mm.,(lit.; 141-148/0.1mm.). The purified product (36; R = H) crystallised on cooling.

Yield: 30.4 gm., (lit.; 30gm., 86.5%)

C,VII,3. 2:3-cycloPenteno-5-keto-5:6:7:8-tetrahydronaphthalene.

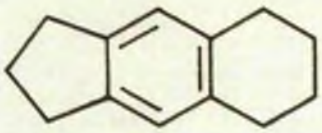


(37)

γ-(5-indanyl)Butyric acid (95gm.)(36; R = H) and a solution of conc. sulphuric acid (330ml.) and water (85ml.) were heated on the steam bath for 3 hours in order to effect cyclodehydration. The reaction mixture was treated with an excess of crushed ice and water, and the organic material taken up in ethereal solution prior to processing in the usual manner. The ketone (37) was obtained as a colourless oil by distillation under reduced pressure, b.p., 140°/0.7mm., (lit.; 92-94°/0.03mm.).

Yield: 70 gm., (lit.; 68gm., 80%)

C,VII,4. 2:3-cycloPenteno-5:6:7:8-tetrahydronaphthalene.



(38)

This preparation is based on the work of Keller[8].

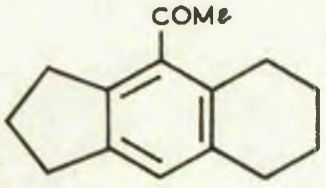
2:3-cycloPenteno-5-keto-5:6:7:8-tetrahydronaphthalene (37; C,VII,3) (15gm.) dissolved in A.R. acetic acid (150ml.) containing A.R. perchloric acid (2ml.) was subjected to catalytic hydrogenation at atmospheric pressure in the presence of Adam's platinium oxide catalyst (250mgm.). The required volume of hydrogen (3.6 litres) was observed to have been absorbed after 4 hours.

The acid solution was added to an excess of water, and the precipitated organic material was taken up in ether and processed in the usual fashion. After removal of solvent by evaporation, the residue was distilled under reduced pressure to give 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38) as a colourless oil.

Yield: 11.9 gm., (86.2%)

B.p.: 98-100°/1.2mm.

C,VII,5. 1-Acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene. (First preparation).



(39)

A solution of acetyl chloride (8.5gm., 5.8ml.) and aluminium chloride (14.2gm.) in 1:2-dichlorethane (100ml.) was added to a well-stirred solution of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (17.5gm.) in 1:2-dichlorethane (100ml.) during the course of half-an-hour at room temperature. The resulting homogeneous solution, which was intensely orange-brown in colour, was allowed to stand at room temperature for a further 2 hours.

The metal-organic complex was decomposed by addition to an excess of 5N. hydrochloric acid, whereupon the liberated organic material and solvent were taken up in an excess of ether to facilitate washing. After processing of the ether solution in the usual fashion, the solvent was removed by evaporation. On distillation of the residue under reduced pressure, the product (39) was obtained as a colourless oil which partly crystallised at room temperature(note 1).

Yield: 19.1 gm., (87.6%)

B.p.: 146-150°/1.3mm.

Analysis: Found; C, 84.0; H, 8.5%

$C_{15}H_{18}O$ requires; C, 84.1; H, 8.5%

A 2:4-dinitrophenylhydrazone of (39) was prepared by boiling a solution containing equimolar quantities of the reactants for 5 minutes followed by the addition of a catalytic quantity of conc. hydrochloric acid. The derivative as obtained in the form of orange needles by

crystallisation from N:N-dimethylformamide.

M.p.: 212-214°

Analysis: Found; C, 63.9; H, 5.6; N, 14.2%

$C_{21}H_{22}N_4O_4$ requires; C, 63.9; H, 5.6; N, 14.2%

Note 1. In an identical preparation using 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (20gm.), aluminium chloride (15.52gm.) and acetyl chloride (9.07gm., 8.19ml.), distillation under reduced pressure gave a total of 20.33gm. of product at 134-138°/0.7mm. Redistillation of the latter yielded two fractions; i.e., 10.22gm. boiling at 138-140°/0.7mm. and 8.78gm. boiling at 140-142°/0.7mm. The second fraction partly crystallised, and was triturated with light petrol to effect removal of crystalline material. In this manner a solid product was obtained in the form of white needles.

Yield: 0.33 gm.

M.p.: 97-99.5°

Analysis: Found; C,84.1 ; H, 8.4%

$C_{15}H_{18}O$ requires; C, 84.1; H, 8.5%

A 2:4-dinitrophenylhydrazone of the solid ketone was prepared by boiling an ethanolic solution containing equimolar quantities of the reactants in the presence of a catalytic quantity of hydrochloric acid. The derivative was obtained in the form of yellow-orange needles by crystallisation (twice) from acetic acid.

M.p.: 218-220°

Analysis: Found; C, 63.5; H, 5.3; N, 13.7%

$C_{21}H_{22}O_4N_4$ requires; C, 63.9; H, 5.62; N, 14.2%

C,VII,6. 1-Acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene. (Second preparation).

A solution of acetyl chloride (7gm., 4.8ml.; 10% excess) and stannic chloride (22gm., 10ml.; 50% excess) in 1:2-dichlorethane (50ml.) was added to a rapidly stirred solution of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38) (10gm.) in 1:2-dichlorethane (50ml.) at room temperature during the course of 30 minutes. The resultant homogeneous solution, which was intensely brown in colour, was allowed to stand for 30 minutes and then boiled under reflux for 1 hour.

The reaction mixture was treated with an excess of 5N. hydrochloric acid to decompose the metal-organic complex, and the solvent and liberated organic material were taken up in an excess of ether prior to processing in the usual manner. After removal of solvent by evaporation, distillation of the residue under reduced pressure yielded the product as an almost colourless oil.

Yield: 8.25 gm., (66%)
B.p.: 148-152°/1mm.

C,VII,7. 1-Acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene. (Third preparation).

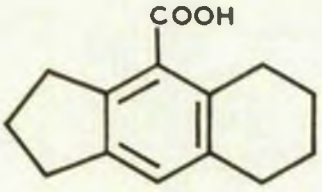
A solution of acetyl chloride (6.55gm., 4.4ml.) and stannic chloride (15.05gm., 6.75ml.) in nitrobenzene (50ml.) was added to a rapidly stirred solution of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38) (10gm.) in nitrobenzene (50ml.) at room temperature during the course of 30 minutes. The resultant homogeneous solution, which was deep orange-brown in colour, was permitted to stand for 1 hour at room temperature.

The reaction mixture was treated with an excess of 5N. hydrochloric acid to decompose the metal-organic complex, and the solvent

and liberated organic material were taken up in an excess of ether prior to processing in the usual fashion. The ether was removed by evaporation and the nitrobenzene taken off by distillation under reduced pressure. Thereafter distillation of the residue gave the product as a pale yellow oil.

Yield:	7.3 gm., (58.5%)
B.p.:	140-144°/1mm.

C,VII,8. 2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid (First preparation).



(40)

A solution of sodium hypochlorite was prepared as follows. Gaseous chlorine was passed through a solution of sodium hydroxide (13.7gm.) in water (30ml.) containing crushed ice (80gm.) until 10.1gm. of gas had been absorbed. At this point the heat of solution had been sufficient to melt all the ice, and a solution of sodium hydroxide (2.5gm.) in water (5ml.) was added.

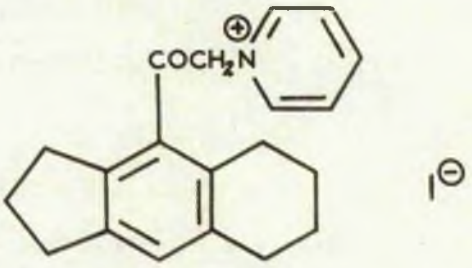
1-Acetyl-2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene (39; the product from preparation C,VII,5) (7gm.) was added to the above solution in one portion, and the resultant suspension was heated under reflux with stirring for 2 hours. On cooling a considerable quantity of brown oil (unreacted ketone) remained undissolved, and this was taken up in ether. The homogeneous aqueous phase was acidified with dilute hydrochloric acid, and the resulting precipitate of crude acid removed by filtration, washed with a small volume of water, and treated

with an excess of boiling sodium bicarbonate solution. Undissolved oily material was removed by extraction with ether, and the acid recovered by acidification of the alkaline solution.

The crude product, dried at 110°, was sublimed under reduced pressure (ca. 1mm.) at 230°, and thus yielded the acid (40) in the form of small colourless needles.

Yield: 2 gm., (28.3%)
M.p.: 129-160°

C,VII,9. 2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid (Second preparation).



(41)

A solution of 1-acetyl-2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene (39; the product from preparation C,VII,5) (10.6gm.) and iodine (12.9gm.) in pyridine (50ml.) was treated in an identical fashion to that described in (C,VII,1). The pure pyridine salt (41) was obtained in the form of orange-coloured needles by crystallisation from ethanol.

Yield: 11.0 gm., (53%)
M.p.: Above 350° (crystals became intensely dark over the range 250-300°, but retained their form).
Analysis: Found; C, 57.6; H, 5.5; N, 3.1; I, 30.0%
$C_{20}H_{22}ONI$ requires; C, 57.3; H, 5.2; N, 3.3; I, 29.6%

The above pyridinium salt (41) (8gm.) was hydrolytically cleaved by treatment with a boiling 50% ethanolic solution (100ml.) containing potassium hydroxide (10gm.) during the course of 2 hours. The crude acid was obtained in a similar manner to that described in (C,VII,1). On sublimation of the latter under reduced pressure (ca. 1mm.) at 200°, the pure product (40) was obtained in the form of colourless plates by crystallisation from methanol.

Yield:	1.8 gm., (43.5%)
M.p.:	222-224° (with sublimation).
Analysis:	Found; C, 77.9; H, 7.7%
	$C_{14}H_{16}O_2$ requires; C, 77.8; H, 7.5%

C,VII,10. 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid: Attempted Dehydrogenation (First experiment).

A distilled ethereal solution of diazomethane was added portionwise to a suspension of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (40; the product from preparation C,VII,9) (0.7gm.) in ether (25ml.) until the acid was entirely consumed by esterification and the colour of the reagent was not discharged on further addition. Polymeric material from the spontaneous decomposition of diazomethane was removed by filtration from the homogeneous ester solution. Removal of solvent by evaporation gave the ester as an almost colourless oil.

A suspension of palladised charcoal (10%) (0.25gm.) in the above oil was heated gradually to 300° during the course of 90 minutes, and maintained at the latter temperature for a further 30 minutes. Gas evolution was observed to commence at 250°, and became negligible after the period of heating at 300°. The cold reaction mixture was exhaustively extracted with boiling methanol (4 x 25ml. portions). An equal volume of water, and potassium hydroxide (5gm.) was added to

the filtered ester solution, and the resulting solution was boiled under reflux for 1 hour to effect hydrolysis. After removal of the bulk of the methanol by distillation, acidic material was precipitated by the addition of dilute hydrochloric acid.

The precipitate was removed by filtration, washed with a small volume of water, and treated with an excess of boiling sodium bicarbonate solution. The crude acid was recovered from the filtered sodium bicarbonate solution by acidification, and subsequently dried at 110°. The dried product was subjected to sublimation under reduced pressure (ca. 1mm.) at 200°. The sublimate on crystallisation from ethanol gave the purified acid in the form of what was observed under the microscope to be a mixture of colourless needles and plates.

Yield:	0.5gm., (73%)
M.p.:	183-217.5° (darkening after 200°).

As the above reaction appeared to have given an inhomogeneous product, the latter was processed again to determine whether dehydrogenation was incomplete. An identical procedure to that previously described was adopted, with the exception that the temperature of the dehydrogenation reaction was raised to 350°., but no appreciable evolution of gas was observed. On working-up of the reaction mixture an acid was obtained which showed no significant alteration in melting point or physical appearance.

C,VII,11. 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid (Third preparation).

A solution of 1-acetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (39; product from preparation C,VII,6) (8gm.) and iodine (9.75gm.) in pyridine (50ml.) was boiled under reflux for 2 hours, during the course of which a brown crystalline mass of crude pyridinium

salt was deposited. The cold reaction mixture was added to an excess of ether, and the precipitated material removed by filtration and washed free of pyridine by a copious volume of ether. The crude product obtained in this manner was used directly without further purification.

A solution of the above in water (50ml.) and ethanol (50ml.) containing potassium hydroxide (10gm.) was boiled under reflux for 2 hours in order to effect hydrolytic cleavage. The bulk of the alcohol was removed from the resulting dark brown solution by distillation, and the crude acid obtained contaminated with a considerable quantity of dark tarry material, by acidification with dilute hydrochloric acid. Preliminary purification was effected by treatment of the precipitate with an excess of boiling sodium bicarbonate solution, screening of the filtered alkaline extract with decolourising carbon, and recovery of the acid by acidification. The partially purified product was dried at 110° and subjected to sublimation under reduced pressure at 230°. The acid was obtained in the form of colourless needles by crystallisation from methanol.

Yield: 1.1 gm., (13.7% overall).
M.p.: 161-171° (softening was observed over the range 146-161° together with sublimation).

C,VII,12. 2:3-cyclopentano-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid (Fourth preparation).

A solution of 1-acetyl-2:3:-cyclopentano-5:6:7:8-tetrahydronaphthalene (39; product from preparation C,VII,7) (7gm.) and iodine (8.5gm.) in pyridine (50ml.) was boiled under reflux for 2 hours. The subsequent procedure was entirely identical to that described in (C,VII,11). The acid resulting from sublimation was obtained in the form of colourless plates by crystallisation from ethanol (note 1).

Yield: 0.667 gm., (9.4% overall).

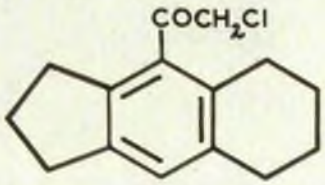
M.p.: 136.5-172.5°

Note 1. On examination under the microscope the recrystallised material was found to comprise both plates and a lesser quantity of needles. The needles partly sublimed and commenced to soften at 150°. The specimen was observed to display monotropy, however, for by 200° all the liquid had resolidified to a solid mass of plates. The stable modification eventually melted over the range 213-231°.

From the mother liquors of the above were obtained colourless needles which melted over the range 150-172°, and the resulting liquid showed no tendency to resolidify at higher temperatures.

The high-melting fraction was recrystallised once again from ethanol, and the resulting product was obtained in the form of plates which did not display monotropy, but which softened over the range 213-234.5°, and finally melted between 234.5-244°.

C,VII,13. 1-Chloracetyl-2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene.



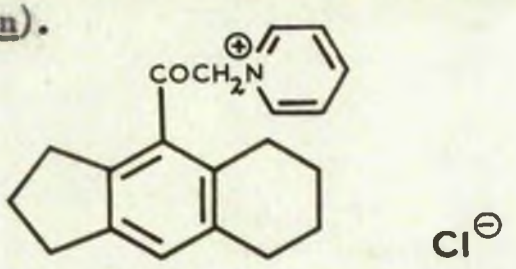
(42)

A solution of chloracetyl chloride (8gm., 5.3ml.) and aluminium chloride (9gm.) in 1:2-dichlorethane (75ml.) was added to a well-stirred solution of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38) (11gm.) in 1:2-dichlorethane (75ml.) at room temperature during the course of 30 minutes. The resulting homogeneous, intensely red solution was allowed to stand at room temperature for a further 2 hours, and subsequently treated with an excess of 5N hydrochloric acid to decompose the metal-organic complex.

The solvent and liberated organic material was taken up in ether solution which was subsequently washed with water (three times) and dried over anhydrous sodium sulphate. After removal of solvent by evaporation, the colourless oil obtained by distillation of the residue under reduced pressure solidified on cooling. The solid crystallised in the form of colourless needles.

Yield:	10.9 gm.
M.p.:	45–65°, (b.p. 170–174°/1mm.)

C,VII,14. 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid. (Fifth preparation).



(43)

A solution of the product from (C,VII,13) (10.9gm.) and pyridine (10ml.) in absolute ethanol (40ml.) was boiled under reflux for 20 minutes and then added to an excess of ether, whereupon the colourless pyridinium salt (43) crystallised immediately.

Yield:	2.5 gm., (theoretical yield 14.4gm.).
M.p.:	240–245° (appreciable darkening was observed after 220° and softening occured over the range 227–240°).

Solvent was removed by evaporation from the ethereal mother liquors, and the residue distilled under reduced pressure to give a colourless oil which solidified on cooling.

Yield:	7.5 gm.
M.p.:	65–75°, (b.p. 170°/1mm.)

The pyridinium salt (43) was hydrolytically cleaved by treatment with boiling aqueous 10% potassium hydroxide solution (100ml.) during the course of 90 minutes. Oily material, which was deposited as a result of the reaction, was taken up in ether, and crude acid precipitated from the alkaline solution by acidification with dilute hydrochloric acid. The precipitate was taken up in an excess of boiling aqueous sodium bicarbonate solution, and after filtration of the latter, the partially purified product was recovered by acidification. After drying at 110° pure material was obtained in the form of colourless compact needles by sublimation under reduced pressure.

Yield:	0.93 gm., (69%)
M.p.:	155-173° (with sublimation).

C,VII,15. 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid: Attempted Dehydrogenation (Second experiment).

A distilled ethereal solution of diazomethane was added portionwise to a suspension of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene carboxylic acid (40; the product from preparation C,VII,14) (0.8gm.) in ether (25ml.) until the acid was entirely consumed by esterification and the colour of the former reagent was not discharged on further addition. Polymeric material from the spontaneous decomposition of diazomethane was removed by filtration of the homogeneous ester solution. Removal of solvent by evaporation gave the ester as an almost colourless oil.

Powdered sulphur (1gm.) was added portionwise to the ester whose temperature was raised progressively from 150° to 300° during the course of 90 minutes. Evolution of hydrogen sulphide was observed to commence at 180° and became negligible at the close of the period of heating. The cold reaction mixture was exhaustively extracted with boiling methanol. An equal volume of water, and potassium hydroxide (5gm.) was

added to the filtered ester solution, and the resulting solution boiled for 1 hour under reflux. After removal of the bulk of the methanol by distillation, acidic material was precipitated by the addition of excess dilute hydrochloric acid.

The precipitate was removed by filtration, washed with a small volume of water, and treated with an excess of boiling sodium bicarbonate solution. The crude acid was regenerated from the filtered sodium bicarbonate solution by acidification, and subsequently dried at 110°. The product, obtained by sublimation under reduced pressure at 200°, on crystallisation from ethanol gave the purified acid in what was observed to be a mixture of plates and needles.

Yield:	5.5 gm., (63%)
M.p.:	133-212° (darkening commenced at 170°. The sample partially resolidified in the form of plates at ca. 194°).

C,VII,16. 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid: (Sixth preparation).

A solution of 2:3-cyclopenteno-5:6:7:8-tetrahydronaphthalene (38; C,VII,4) (2gm.) and oxalyl chloride (1.5gm., 1ml.) in nitrobenzene (25ml.) was heated in such a manner that its temperature was raised from 100° to the boiling point of the solvent during the course of 6 hours. The cold reaction mixture was taken up in an excess of ether, and the latter extracted with sodium bicarbonate solution. No material was deposited on acidification of the alkaline extracts.

The above ethereal solution was washed once with water and dried over anhydrous sodium sulphate. After evaporation of the ether, 20% of the total volume of nitrobenzene in the residual solution was removed by distillation in order to render the latter anhydrous.

Oxalyl chloride (1.5gm., 1ml.) and aluminium chloride (1.5gm.) dissolved in nitrobenzene (10ml.) were added in one portion to the above, and the whole allowed to stand at room temperature for 2 hours. Thereupon the reaction mixture was poured into an excess of 5N. hydrochloric acid to decompose the metal-organic complex, and solvent and regenerated organic material were taken up in an excess of ether. The latter was washed twice with water, and then extracted with two portions of 10% potassium hydroxide solution. A small quantity of material was deposited on acidification of the alkaline extracts, and this was removed by filtration, washed once with water, and taken up in an excess of boiling sodium bicarbonate solution. The acid was regenerated by acidification, and dried at 110°. The pure product was obtained in the form of very pale yellow prisms by recrystallisation from ethanol.

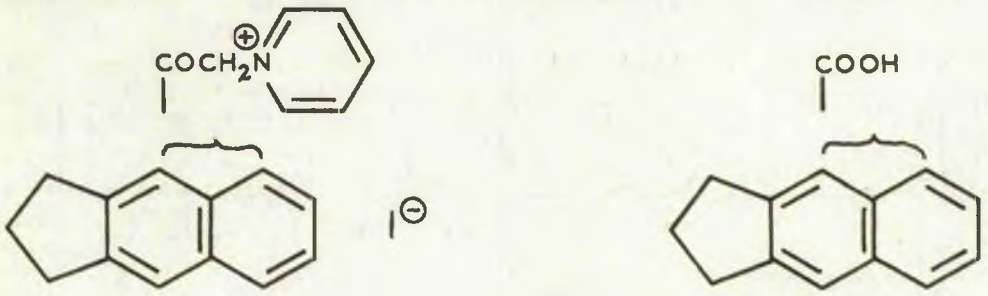
Yield: 0.27 gm., (10.8%)

M.p.: 235.5-237.5° (darkening at m.p.).

Analysis: Found; C, 77.8; H, 7.6%

$C_{14}H_{16}O_2$ requires; C, 77.8; H, 7.4%

6,VII,17. 2:3-cyclePentenonaphthalene Carboxylic Acid.



(44) (45)

A solution of acetyl-2:3-cyclopentenonaphthalene (C,VI,1) (10gm.) and iodine (12.1gm.) was boiled under reflux for 2 hours, during which time a brown crystalline mass consisting of the crude pyridinium salts (44) contaminated with a considerable quantity of other pyridinium salts was deposited. To complete precipitation

the reaction mixture was poured into an excess of ether at the end of the period of heating. The precipitate was filtered, washed free of pyridine with ether, and exhaustively extracted with boiling ethanol (in which the pyridinium salt is sparingly soluble but the contaminants completely insoluble). The ethanolic filtrates were concentrated to low volume prior to crystallisation of the crude salt as a tan-coloured powder. A further crystallisation from ethanol, involving treatment with decolourising charcoal, gave the product in the form of pale yellow needles. An analytically pure specimen was obtained by further crystallisation from ethanol (twice), and screening with decolourising charcoal (once).

Yield: 7 gm., (35.5%)

M.p.: 241-246° (decomp.; slow darkening occurred after 200°).

Analysis: Found; C, 58.4; H, 4.5; N, 3.5; I, 30.5%

$C_{20}H_{18}ONI$ requires; C, 57.8; H, 4.4; N, 3.4; I, 30.6%

The pyridinium salt (44) was hydrolytically cleaved by boiling under reflux a solution of the latter (5gm.) in 50% ethanol (100ml.) containing potassium hydroxide (10gm.) for 2 hours. Water(50ml.) was added to the solution which was dense brown in colour, and the bulk of the alcohol removed by distillation. On acidification the crude acid (45) was obtained accompanied by a considerable amount of brown oily material. Preliminary purification was effected by extracting the crude mixture with sodium bicarbonate solution and treatment of the latter with decolourising carbon. On acidification a somewhat purer product was obtained, which was air-dried and then subjected to sublimation under reduced pressure (ca. 1mm.). The pure cyclopenteno-naphthalene carboxylic acid crystallised in the form of colourless needles from benzene:acetone mixture (2:1).

Yield: 1.17 gm., (46.0%)

M.p.: 194.5-196.5°

Analysis: Found; C, 79.0; H, 5.2%

$C_{14}H_{12}O_{12}$ requires; C, 79.2; H, 5.7%

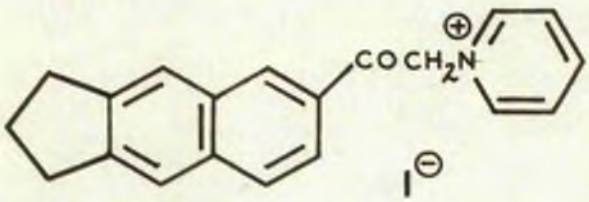
The acid chloride was prepared by interaction of the acid (45) and thionyl chloride, followed by removal of excess of the latter by distillation. The residue was treated with concentrated ammonia solution, and the resulting crude amide filtered off and extracted with sodium bicarbonate to remove unchanged acid. The crude product was air-dried and sublimed under reduced pressure (ca. 1mm.), whence the pure amide corresponding to acid (45) was obtained in the form of colourless needles.

M.p.: 140.5-142°

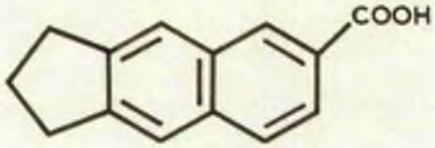
Analysis: Found; C, 79.5; H, 6.2; N, 6.5%

$C_{14}H_{13}ON$ requires; C, 79.6; H, 6.2; N, 6.6%

C,VII,18. 2:3-cyclopentenonaphthalene-7-carboxylic Acid.



(46)



(47)

A solution of the colourless, solid ketone (29; C,VI,1; note 3) (1.54gm.) and iodine (1.9gm.) in pyridine (10ml.) was treated in an identical fashion to that described in (C,VII,1). The pure pyridinium salt (46) was obtained in the form of pale yellow needles.

Yield: 0.50 gm., (16.5%)

M.p.: 241-242° (with slow heating. Salt turns slowly yellow on heating and becomes orange in colour just before melting.)

243-244.5° (rapid heating.)

Analysis: Found; C, 58.2; H, 4.4; N, 3.35; I, 30.3%

$C_{20}H_{18}ONI$ requires; C, 57.85; H, 4.4; N, 3.4; I, 30.6%

A solution of the pyridinium iodide (46) (0.63gm.) in ethanol:water mixture (2:1)(30ml.) containing potassium hydroxide (1gm.) was treated in essentially the same manner as described in (C,VII,17) in order to effect hydrolytic cleavage. The acid (47) was obtained in the form of colourless plates by crystallisation from ethanol.

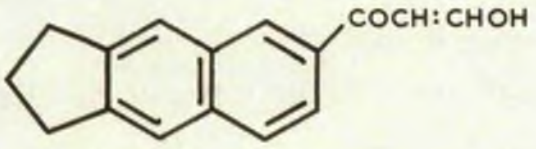
Yield: 0.21 gm., (67.5%)

M.p.: 276-281°

Analysis: Found; C, 79.4; H, 5.4%

$C_{14}H_{12}O_2$ requires; C, 79.2; H, 5.7%

C,VII,19. Oxymethylene Derivative of 7-Acetyl-2:3-cyclopentenonaphthalene.



(48)

Ethyl formate (0.81gm.,0.88ml.; 10% excess) was added to a suspension of anhydrous potassium methoxide (0.77gm.; 10% excess) in a solution of 7-acetyl-2:3-cyclopentenonaphthalene (29; C,VI,1;note 3) (2.1gm.) in sodium dried ether (50ml.). During the course of the addition the reaction mixture warmed spontaneously, after which boiling under

reflux was maintained by external heating for 2 hours. The sodium salt of the oxymethylene derivative was deposited as a voluminous white precipitate.

The reaction mixture was poured in an excess of water and the product extracted into the aqueous phase. The free oxymethylene derivative, generated by acidification, was taken up in ether and processed in the usual fashion. On evaporation of solvent, a pale yellow crystalline solid remained. This was recrystallised twice from carbon tetrachloride yielding the oxymethylene derivative of 7-acetyl-2:3-cyclopentenonaphthalene (48) as pale yellow plates (note 1).

An analytical sample was prepared by recrystallisation of the latter from carbon tetrachloride and then from ethanol. The sample was dried at room temperature under reduced pressure.

Yield:	1.68 gm., (74%)
M.p.:	112-120° (becomes deep yellow at m.p.)
Analysis:	Found; C, 81.0; H, 6.4%
	$C_{15}H_{14}O_2$ requires; C, 80.6; H, 5.9%

Note 1. An attempt was made to cyclodehydrate (48) by the method outlined in (C,VI,3), but no satisfactory product was isolated from the reaction. On this basis the original ketone (29) is formulated with the acetyl group in position 7.

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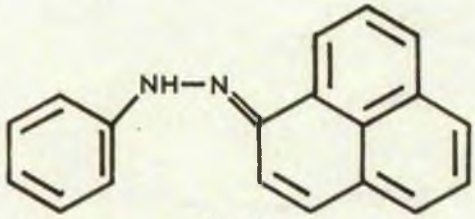
C.VIII. INDOLO[2,3-a]PERINAPHTHENE SALTS.

C.VIII.1. Perinaphthan-1-one Phenylhydrazone.

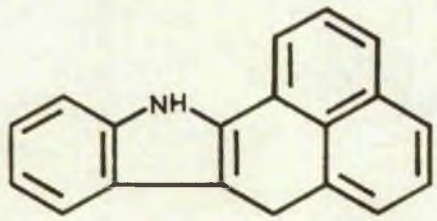


(49)

Perinaphthan-1-one (9.1gm.), phenylhydrazine (5.4gm.) and concentrated hydrochloric acid (0.1ml.) were dissolved in ethanol and boiled under reflux for 5 minutes. On cooling the phenylhydrazine (49) was precipitated from the solution in the form of yellow leaflets. The product was recrystallised once from methanol.

Yield:	10.3 gm., (75.5%)	
M.p.:	89-91°	
Analysis:	Found;	C, 83.7; H, 6.0; N, 10.3%
	$C_{19}H_{16}N_2$ requires;	C, 83.8; H, 5.9; N, 10.3%

C.VIII.2. Indolo[3,2-b]perinaphthene.



(50)

A suspension of perinaphthan-1-one phenylhydrazone (49) (2.5gm.) in acetic acid (15.0ml.) was rapidly raised to boiling under reflux and maintained at this temperature for 2 minutes. On cooling indolo[3,2-b]-perinaphthene (50) was precipitated in the form of brownish prisms.

After recrystallisation from cyclohexane (note 1), the product was obtained as almost colourless plates.

Yield: 0.32 gm., (13.6%)

M.p.: Greater than 100° (note 2).

Analysis: Found; C, 88.9; H, 5.4; N, 5.15%

$C_{19}H_{13}N$ requires; C, 89.4; H, 5.1; N, 5.5%

By mixing filtered ethanolic solutions at boiling point containing equimolecular quantities of the reactants and allowing to cool, a sym-trinitrobenzene complex of (50) was obtained in the form of dark brown needles. The complex was only sparingly soluble in ethanol, but dissolved freely in benzene, the latter solution depositing an insoluble brown gum on exposure to air.

M.p.: 114-116° (decomp.)

Analysis: $C_{19}H_{13}N.\ C_6H_3O_6N_3$ requires; C, 64.1; H, 3.4; N, 12.0%

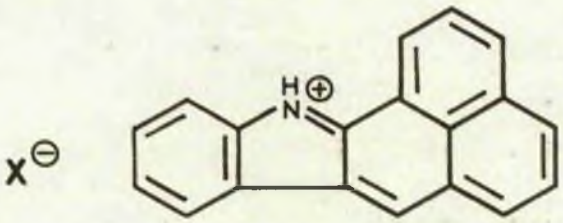
Found; C, 54.3; H, 2.7; N, 12.1%

$C_{19}H_{13}N.2(C_6H_3O_6N_3)$ requires; C, 54.6; H, 3.6; N, 14.4%

Note 1. Solutions of the indole turn red on standing, possibly due to aerial oxidation, and the crystallisation operation must be performed with as much rapidity as possible. In the most satisfactory procedure evolved, the indole was dissolved in near boiling cyclohexane as swiftly as possible, and the solution filtered immediately through a glass funnel. Thereupon crystals were deposited from the filtrate, and this process was assisted by external chilling of the latter. The precipitate of recrystallised material was removed by filtration at once.

Note 2. The indole did not possess a sharp m.p., but became orange at 100°, and then progressively darker on subsequent heating. At higher temperatures softening to a plastic mass occurred, in which individual crystals lacking some of their sharp crystalline form were observable.

C,VIII,3. Indolo[2,3-a]perinaphthene Hydriodide.



(51)

A solution of indolo[3,2-b]perinaphthene (50) (0.400gm.) in acetone (5ml.) was heated to boiling and added to a hot solution of iodine (0.400gm.) in acetone (12ml.) and methanol (8ml.). The mixture was boiled for 1 minute and allowed to cool, whereupon the hydriodide of indolo[2,3-a]perinaphthene (51)(note 1) crystallised spontaneously in the form of violet black needles. The salt (51; X = I) dissolved in methanol or ethanol, giving red solutions, and in chloroform, giving purple-red solutions.

Yield: 0.48 gm., (80%)

M.p.: 233-238° (darkening ca. 220°).

Note 1. Analytical data, which was consistently deficient in all elements in several determinations, indicated that iodide was accompanied by periodide anion.

C,VIII,4. Indolo[2,3-a]perinaphthene Hydroperchlorate. (First preparation).

Perchloric acid (72%)(2ml.) was added to a solution of indolo[2,3-a]-perinaphthene hydriodide (51; C,VIII,3; note 1) (0.50gm.) in methanol (500ml.) and the resulting solution was concentrated by evaporation to 250ml. The perchlorate crystallised readily as small black needles. A further quantity of product (ca. one seventh of the total yield) was obtained by concentration of the mother liquors. Purification was

effected by recrystallisation from methanol (note 1) which gave the salt (51; X = ClO_4) in the form of long brown needles.

Yield: 0.33 gm., (71%)

M.p.: 287-296° (sintering occurred above 250°).

Analysis: Found; N, 3.9; Cl, 9.7%

$C_{19}H_{12}O_4NCl$. requires; N, 4.0; Cl, 10.0%

Note 1. The product dissolves very slowly, and consequently it is more convenient to use an excess of boiling solvent, followed by concentration of the solution prior to crystallisation. Thus in a typical operation, the perchlorate (51; X = ClO_4) (0.28gm.) was dissolved in boiling methanol (250ml.) and the resulting solution reduced to 50ml. in volume by evaporation before crystallisation was attempted.

C.VIII.5. Indolo[2.3-a]perinaphthene Hydroperchlorate. (Second preparation).

Glacial acetic acid (400ml.) was added to a flask containing perinaphthan-1-one phenylhydrazone (15.0gm.)(note 1) from which the air had been displaced by a stream of oxygen-free nitrogen. The latter was maintained throughout the course of the preparation until the stage when the crude product was removed from the reaction mixture by filtration. A.R. Perchloric acid (72%)(10ml.) was added to the above and the resultant mixture heated to boiling. The solution, initially light brown at room temperature, darkened to reddish-brown on the addition of perchloric acid, and eventually became deep red in colour after boiling for a few minutes. The reaction mixture was boiled under reflux for 30 minutes, during the course of which solid crystallised out. After standing for 2 hours in the cold, the crude product, which had separated in the form of black needles, was removed by filtration. The latter was washed with glacial acetic acid, allowed to stand in water (300ml.) for 2 hours and removed by filtration, washed with water,

ether, and finally dried in vacuo (note 2).

The crude material was recrystallised from a large volume of glacial acetic acid containing about 1%(by volume) perchloric acid. Some undissolved solid was removed by filtration of the solution at the boiling point, and on subsequent cooling of the filtrate the salt crystallised in the form of reddish-brown needles (note 3).

Yield:	11.1 gm., (51%)
M.p.:	287-296° (sintering occurred above 250°).
Analysis:	Found; N, 3.9; Cl, 9.7%
	$C_{19}H_{12}O_4N$Cl requires; N, 4.0; Cl, 10.0%

Note 1. The preparation may also be carried out using an appropriate quantity of indolo[3,2-b]perinaphthene (50).

Note 2. A significant quantity of an ammonium salt, presumably ammonium perchlorate, is deposited along with the organic salt. This is successfully removed by allowing the crude product to stand in water.

Note 3. The product (52) is obtained directly in a high degree of purity by the process outlined, and recrystallisation does not result in an effective improvement.

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C.IX. MEASUREMENT OF THE BASICITY OF INDENO[2.1-a]PERINAPHTHENE.

The experimental procedure followed and the results obtained in the determination of the appropriate Hammett function value for indeno[2,1-a]perinaphthene are described below. For the theoretical considerations involved see (B,III,1).

Equal volumes (10ml.) of sulphuric acid of previously determined concentrations and a standard solution of indeno(2,1-a]perinaphthene in cyclohexane were shaken together vigorously to ensure complete distribution of the hydrocarbon between both phases. After allowing the latter to separate a 5ml. portion of the organic solution was diluted with a further 5ml. of solvent prior to determination of its optical density on the spectrophotometer.

Optimum performance of the spectrophotometer is normally obtained utilising solutions which give a resultant optical density of ca. 0.4. The wavelength of the absorption maximum of (6), selected for optical measurements, was 484mμ (ε = 7920). Therefore, in order that the acid-extracted organic solutions in the vicinity of acid concentrations where K' = 1 (when the hydrocarbon is approximately equi-partitioned between the two phases) may possess satisfactory optical densities, it may be shown by simple calculation that the concentration of hydrocarbon in the original standard solution should be of the order of 40mgm./litre. Accordingly a solution consisting of 10mgm. of indeno[2,1-a]perinaphthene in 250ml. of cyclohexane was used in these determinations.

In (B,III,1) K' (the apparent partition coefficient) was defined as in the equation, $K' = C'_B/C_{BH^+}$, where C'_B was the concentration of free base in the organic phase and C_{BH^+} the concentration of the corresponding conjugate in the acid phase. The optical density D of a solution is defined as

$$D = \log (I_o/I) = \varepsilon . c . l.$$

where I_o is the intensity of the incident light, I is the intensity of

.the transmitted light, l the thickness of the absorbing solution, and ε and c respectively the extinction coefficient and concentration of the light-absorbing solute. In the present context, if D represents the optical density of the organic solution after acid extraction, and D_s represents the optical density of the original solution, then from the above it follows that

$$K' = (C'_B/C_{BH^+}) = \frac{D}{(D_s - D)} .$$

A number of preliminary determinations were carried out with a view to assessing the region of acid concentrations wherein the desired value of Ho would fall. Eventually the following five results were selected for the final evaluation of the appropriate Hammett function. The readings were taken at 484mμ and checked at 443mμ.

% H_2SO_4 (w/w)	D	$D_s - D$	$\frac{D}{(D_s - D)}$	$\log \frac{D}{D_s - D}$ (= log K')	H_o
67.63	0.114	1.051	0.109	- 0.965	- 5.25
66.25	0.280	0.885	0.316	- 0.500	- 5.07
63.87	0.636	0.529	1.202	+ 0.080	- 4.75
62.37	0.920	0.245	3.755	+ 0.575	- 4.58
59.78	1.070	0.095	11.27	+ 1.052	- 4.30

The Hammett function values corresponding to the acid concentrations recorded above were obtained from a graph constructed from published data[9]. A plot of log K' against Ho (plate IX) disclosed that the value of the Hammett function, for which K' is unity with reference to indeno[2,1-a]-perinaphthene, is -4.80 (64% sulphuric acid).

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PART C. LITERATURE CITED.

(for explanation of abbreviations used see 'Literature Cited, Part A.)

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(2) Read and Hurst, J.C.S., (1922), 2550.

(3) Walters, Chem. Ind., (1927), 150.

(4) Vollmann, Becker, Corell and Streeck, Ann., 531 (1937), 1.

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(8) Keller, Thesis, (E.T.H. Zurich, 1952), 41 et seq.

(9) Hammett and Paul, J.A.C.S., 56 (1934), 827.

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PLATES.

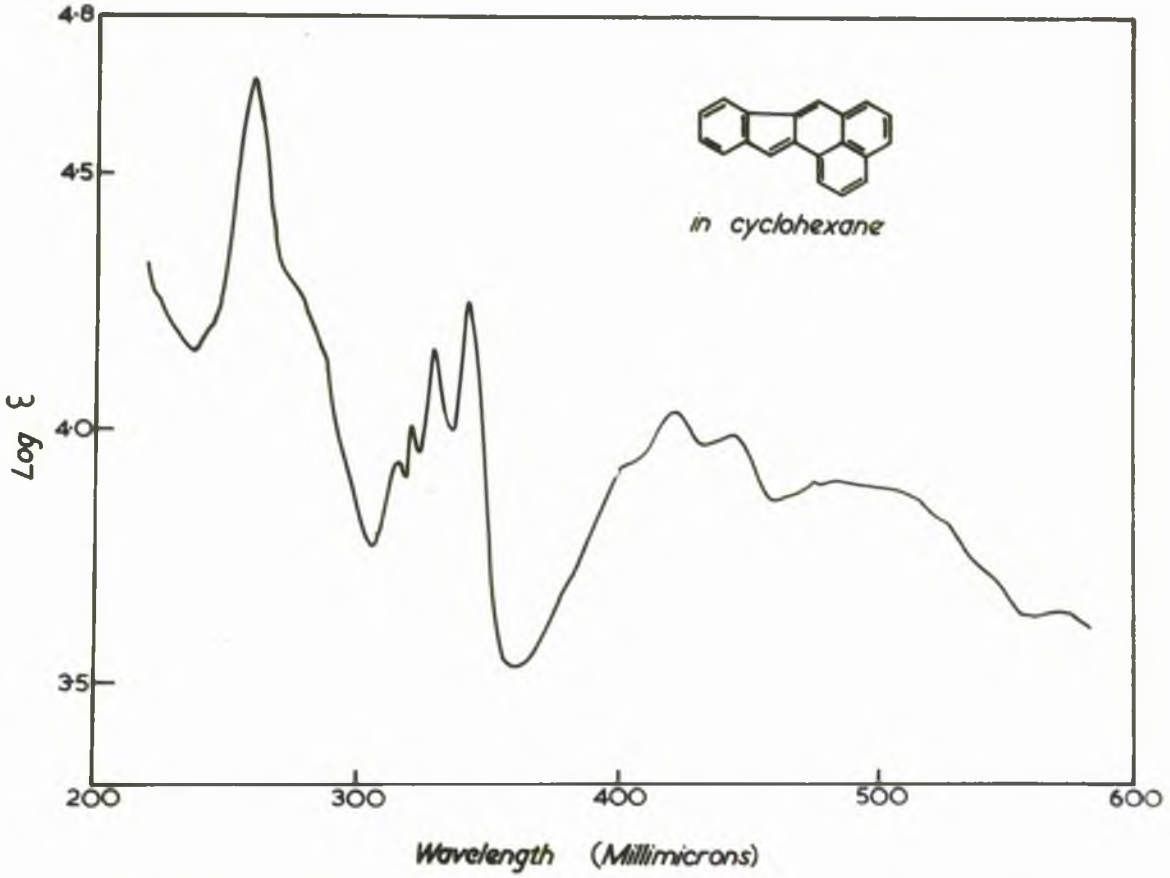

PLATE I Visible and ultra-violet absorption spectrum of indeno-[2,1-a]perinaphthene in cyclohexane.

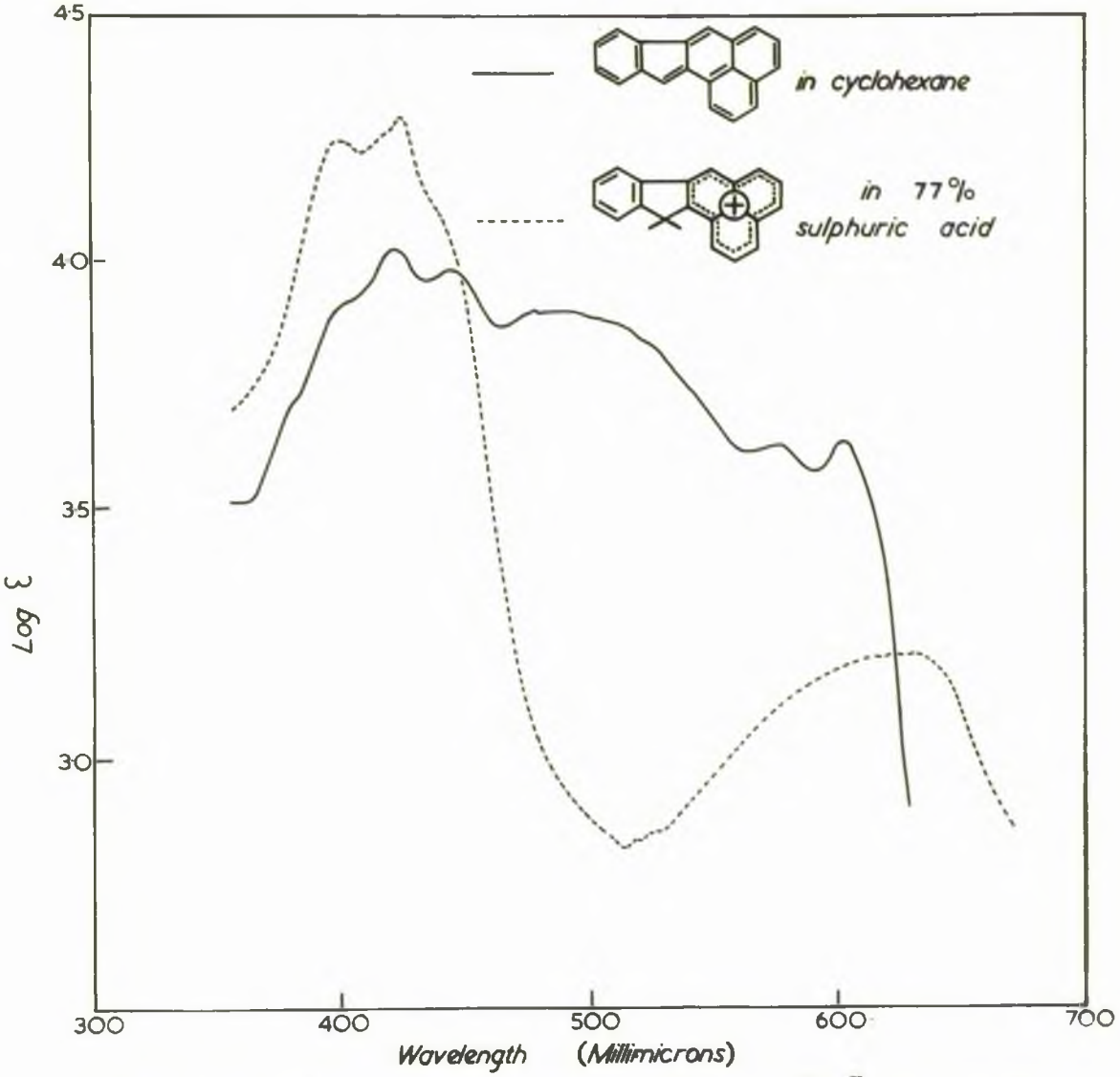

PLATE II. Visible absorption spectrum of indeno[2,1-a]perinaphthene in cyclohexane and 77% sulphuric acid.

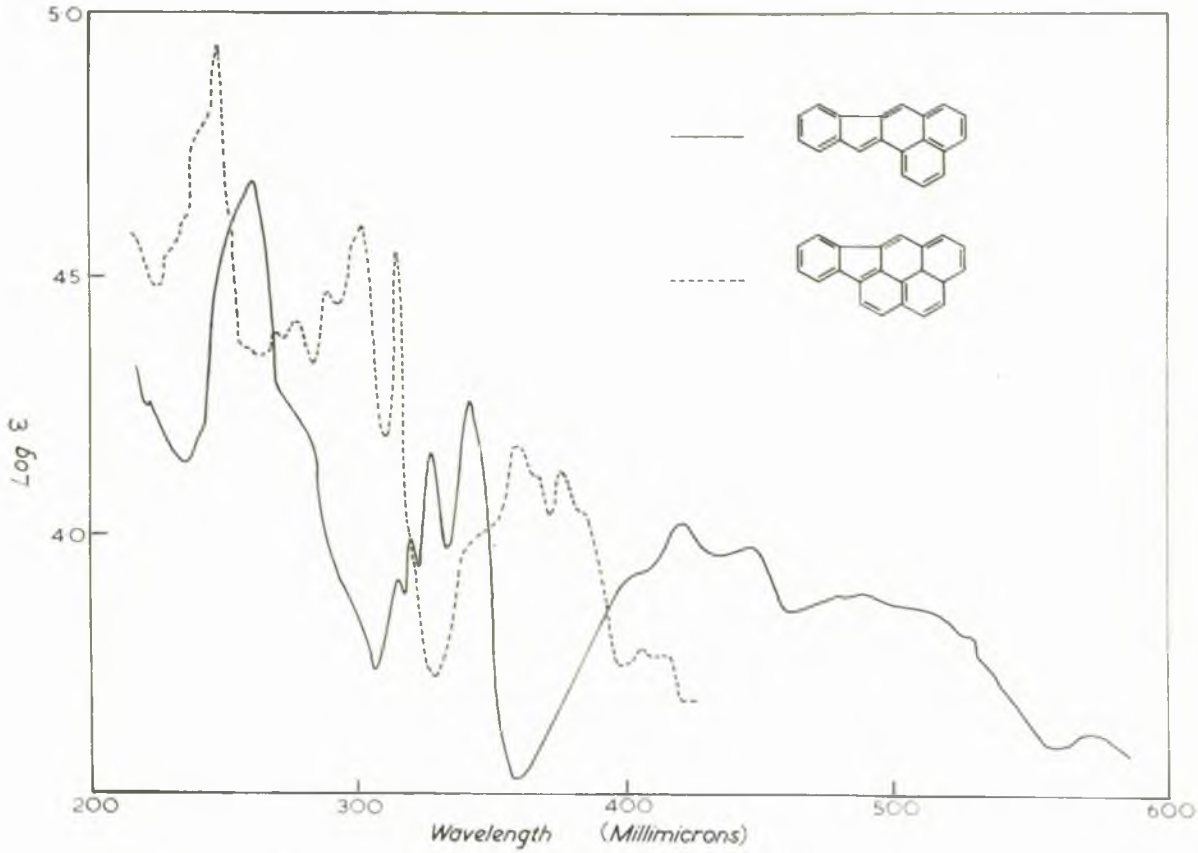

PLATE III. Visible and ultra-violet absorption spectra of indeno[2,1-a] perinaphthene and indeno[1,2,3-cd] pyrene in cyclohexane.

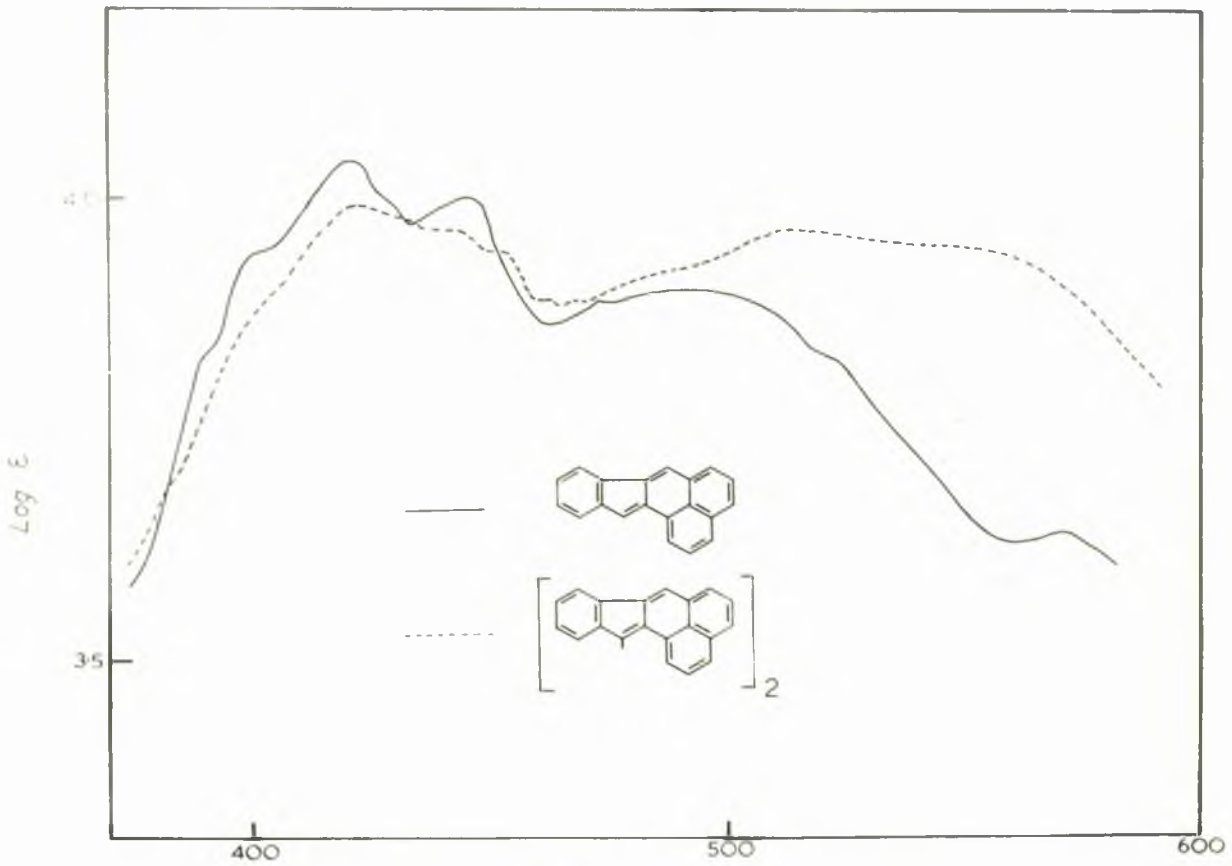

PLATE IV. Visible absorption spectra of indeno[2,1-a]perinaphthene and di(indeno[2,1-a]perinaphthenyl) $(\log \varepsilon/2)$ in benzene

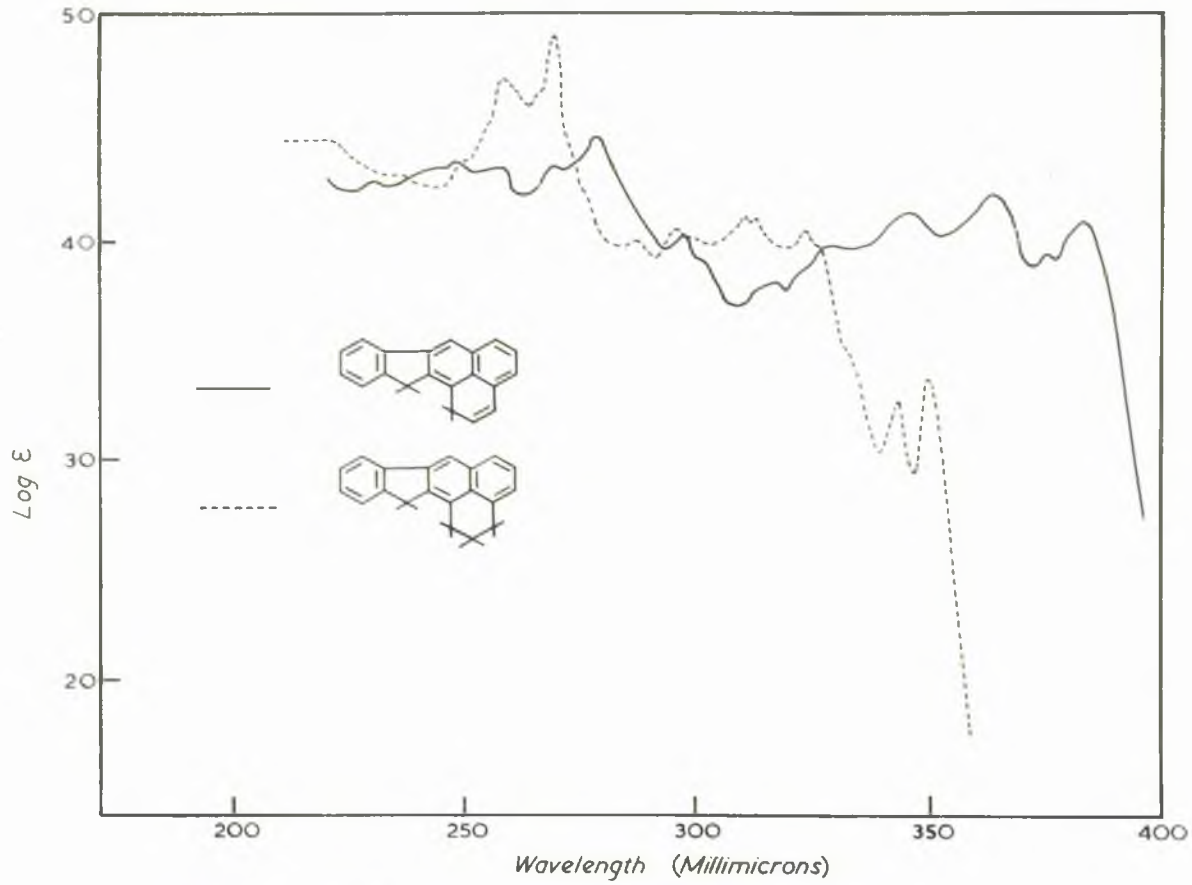

PLATE V. Ultra-violet absorption spectra of dihydro- and tetrahydro-indeno[2,1-a]perinaphthene in cyclohexane.

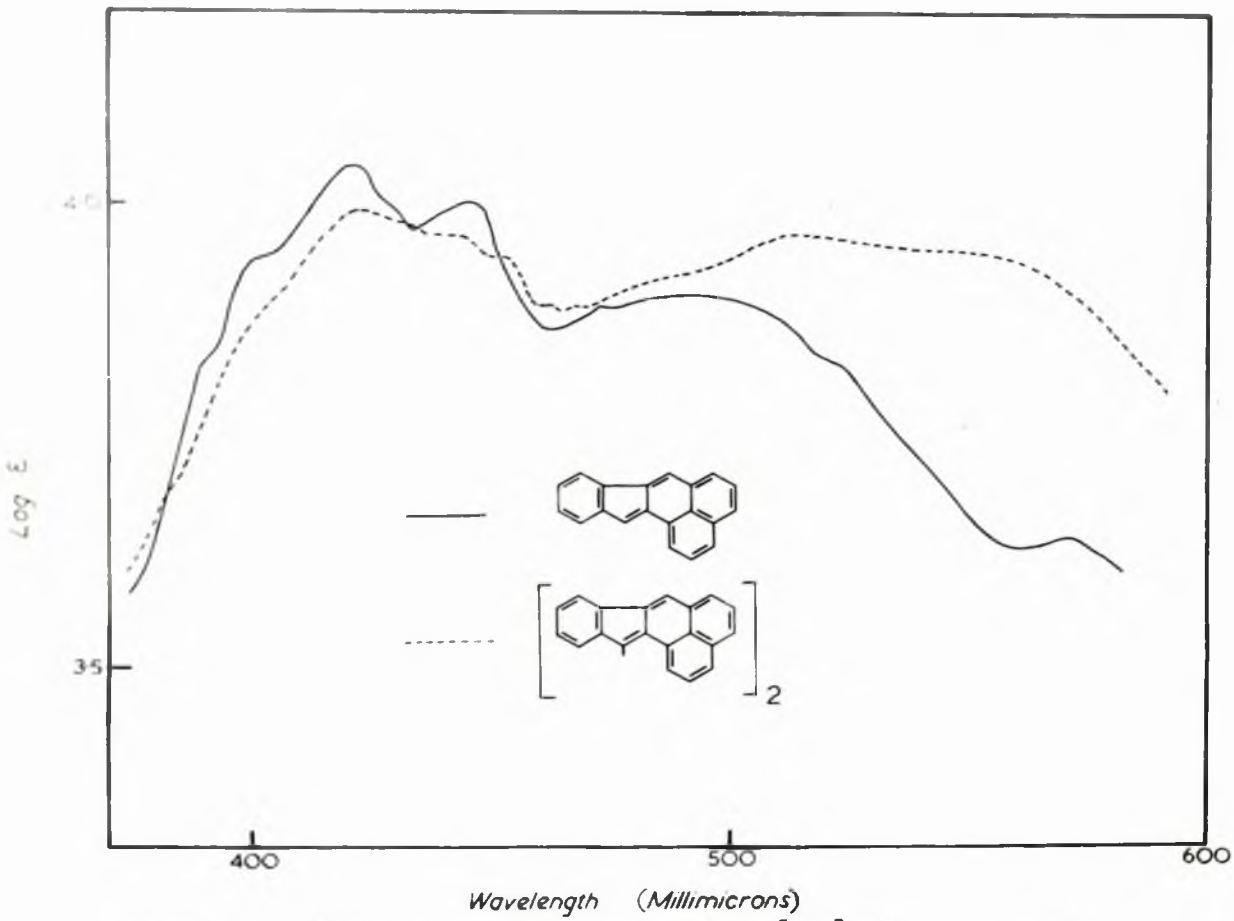

PLATE IV. Visible absorption spectra of indeno[2,1-a]perinaphthene and di(indeno[2,1-a]perinaphthenyl) $(\log \varepsilon/2)$ in benzene.

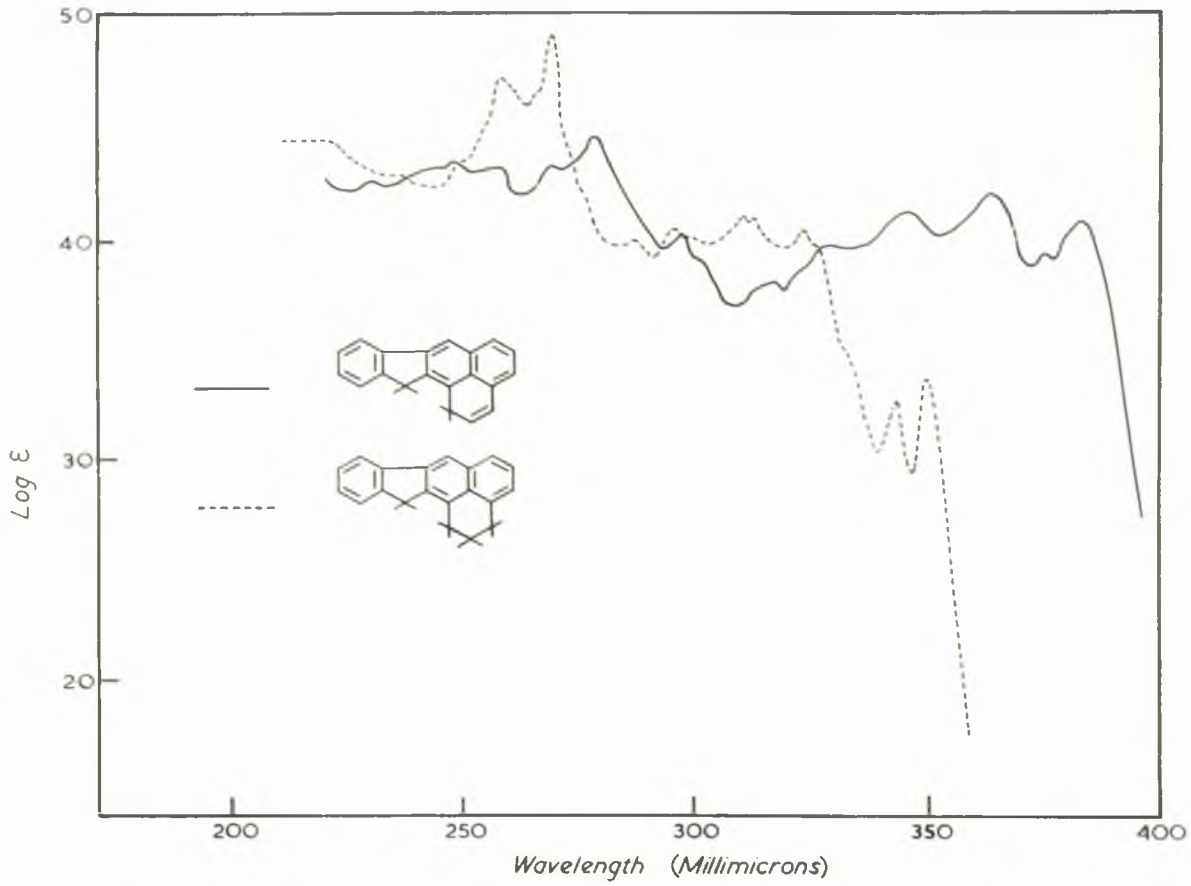

PLATE V. Ultra-violet absorption spectra of dihydro- and tetrahydro-indeno[2,1-a]perinaphthene in cyclohexane.

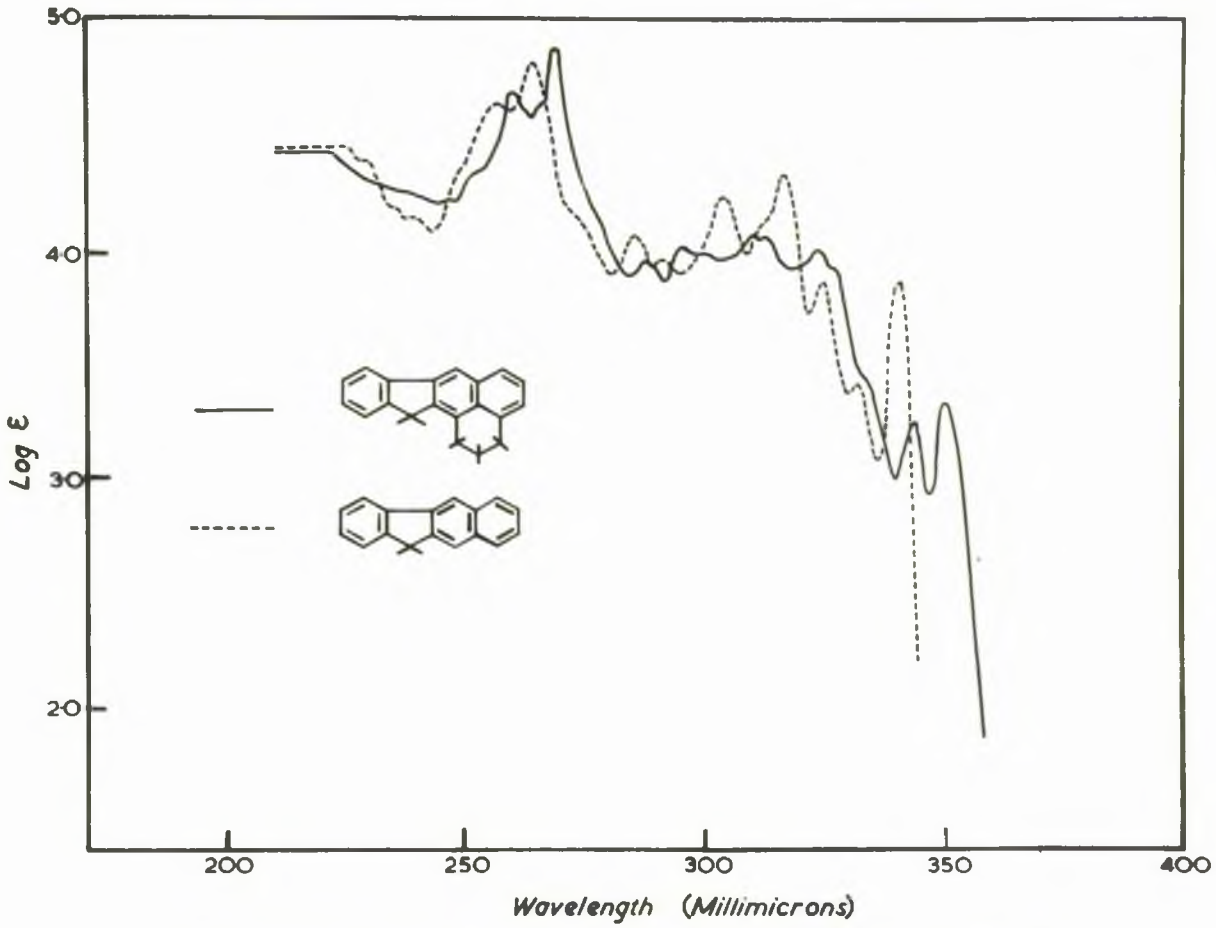

PLATE VI. Ultra-violet absorption spectra of tetrahydro-indeno [2,1-a] peri-naphthene and 2:3-benzfluorene in cyclohexane.

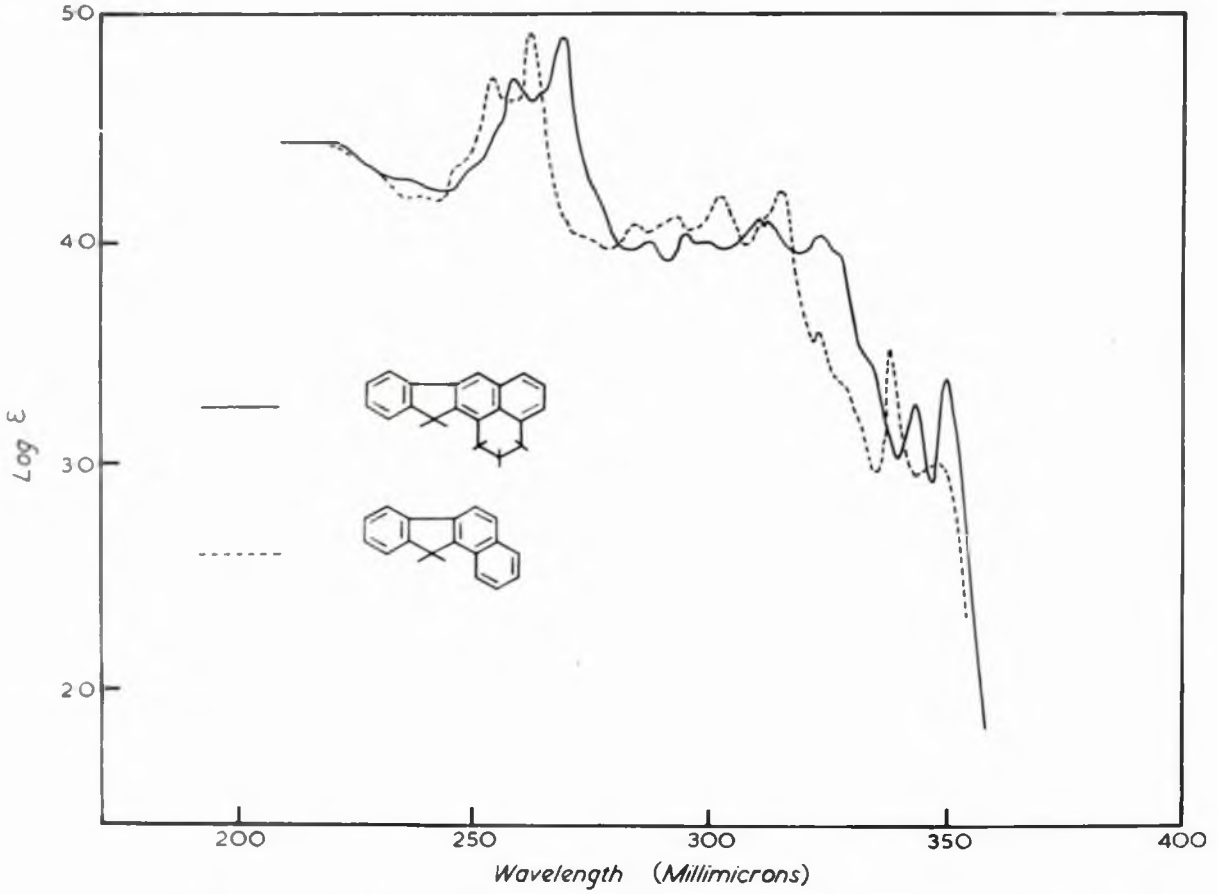

PLATE VII. Ultra-violet absorption spectra of tetrahydro indeno[2,1-a]peri-naphthene and 1:2-benzfluorene in cyclohexane.

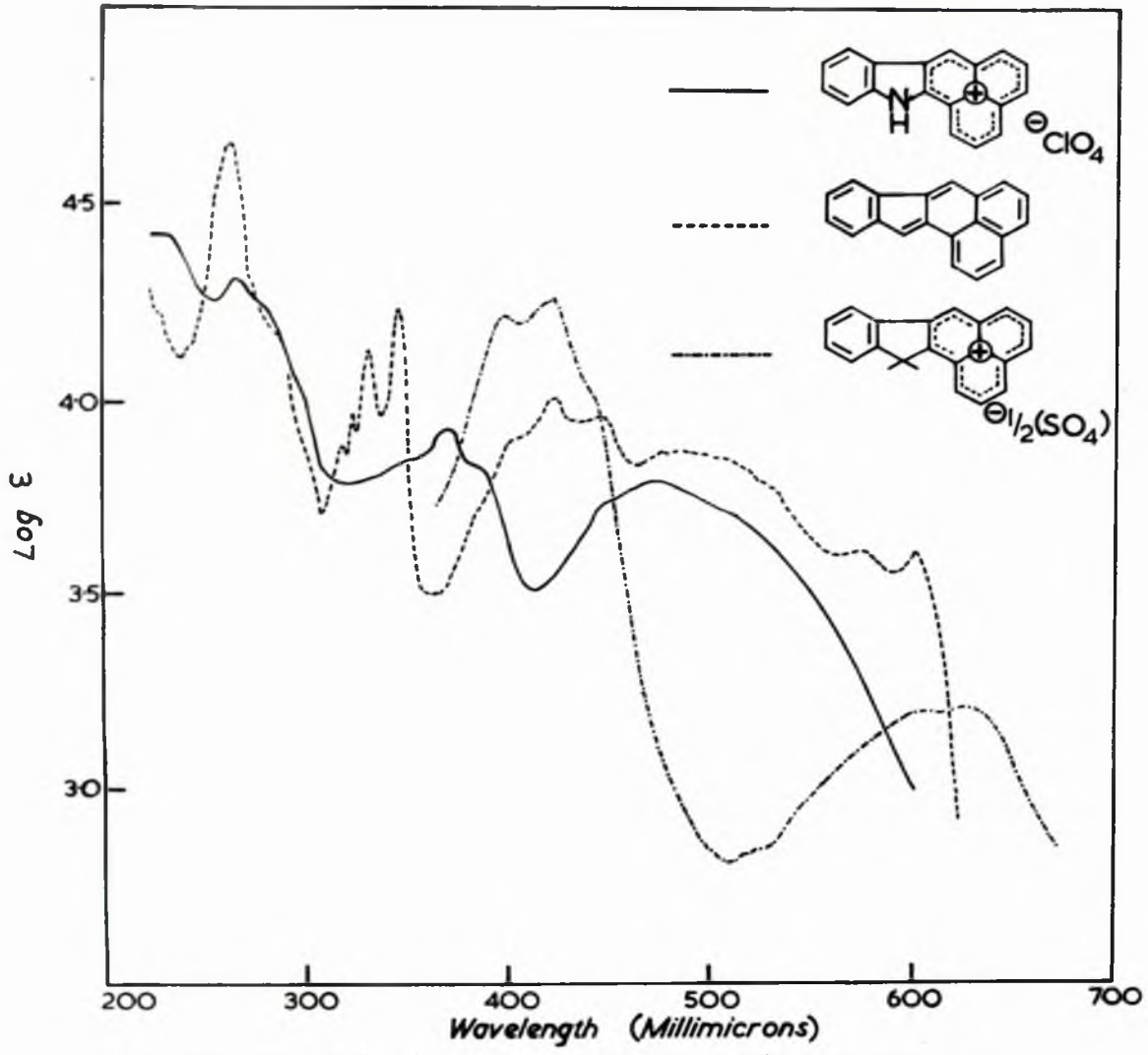

PLATE VIII. Visible and ultra-violet absorption spectra of indolo[2,3-a]perinaphthene perchlorate in methanol, and indeno[2,1-a]perinaphthene in cyclohexane and in 77% sulphuric acid.

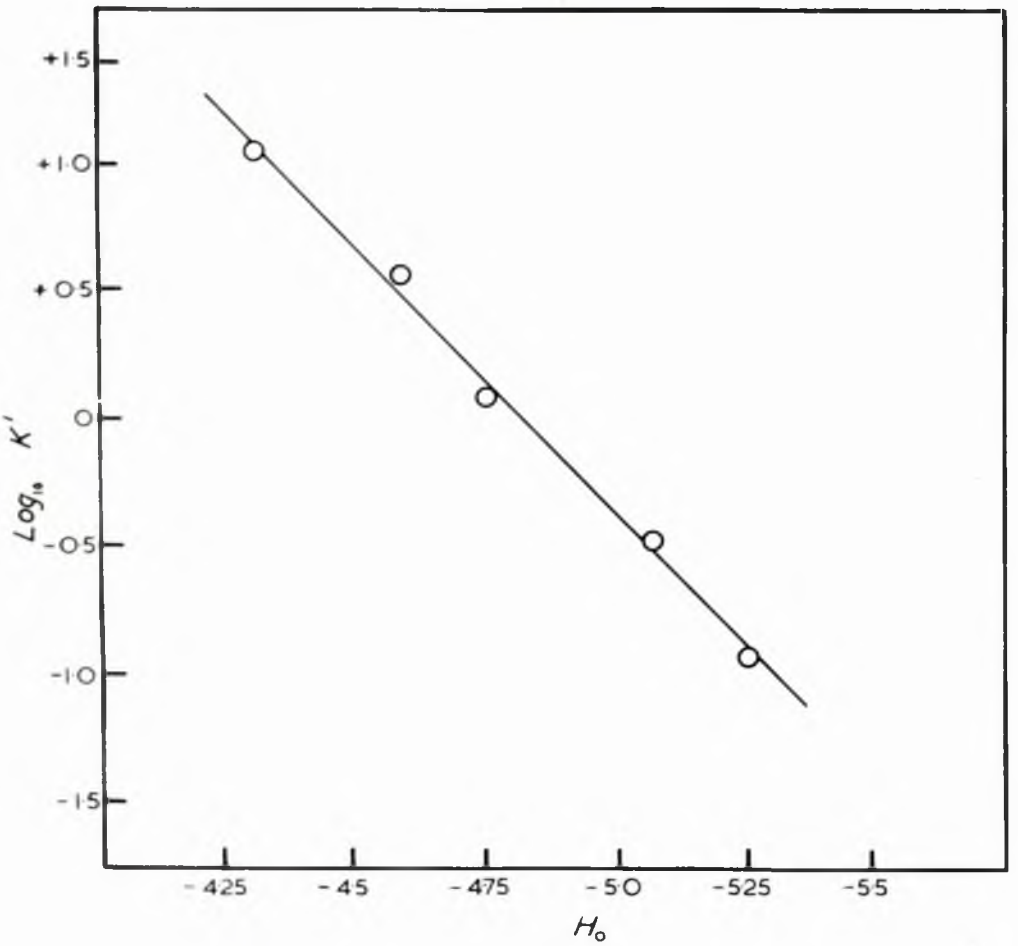

PLATE IX Plot of log_{10} K' (*apparent partition coefficient*) against H_0 (*Hammett acidity function*) for indeno[2,1-a]perinaphthene distributed between cyclohexane and sulphuric acid of different strengths (*slope* = 2·1).